# Metal concentrations in the Suir Estuary as indicated by analysis of biota, sediments and water

Thesis



Link(s) to article on publisher's website:
http://dx.doi.org/doi:10.21954/ou.ro.0000fbd5

UNRESTRICTED

# METAL CONCENTRATIONS

# IN THE SUIR ESTUARY AS INDICATED BY ANALYSIS OF

# BIOTA, SEDIMENTS AND WATER

by

**EDMUND FITZGERALD M. Agr. Sc., N.U.I.**

**A thesis**
**presented to The Open University**
**in fulfilment of the**
**thesis requirement for the degree of**
**Doctor of Philosophy**

**The research was conducted under the auspices of the**
**Department of Environmental and Mechanical Engineering,**
**Faculty of Technology, The Open University,**
**under the supervision of**
**Dr. S. T. Nesaratnam and Dr. J. M. Caffrey**

**2002**

DATE OF SUBMISSION: 23 JANUARY 2002
DATE OF AWARD: 19 JULY 2002

**To Mary, Ruth, Rosemary and Ciara**

*Man did not weave the web of life; he is merely a strand in it. Whatever he does to the strand he does to himself.*

Author unknown

# CONTENTS

# LIST OF FIGURES

# CHAPTER 1

# General Introduction

Estuaries ultimately receive a large proportion of the waste produced by humans that is discharged into aquatic systems. Of major ecotoxicological importance in this waste are metals derived from mining, industrial and agricultural sources (Wilson, 1988; McLuskey, 1989). Long-term contamination by metals can result in the exclusion of a species or population, in the evolution of specific metal-tolerances, or in sub-lethal effects manifesting themselves as a lower growth rate, a lower production of offspring, or other characteristic toxic symptoms (Beeftink, *et al.*, 1982). Despite high concentrations of metals in salt marsh sediments there have been no reports of acute toxicity symptoms in plants (Adam, 1990). Indeed, wetland plants are being used for the removal of metals from contaminated water and for rehabilitation of mine wastes, and this seems to indicate that high metal concentrations do not impose stress on these plants (Otte, 2001). An important advantage of using biota (including plants), for monitoring of metal contamination, is that metal concentrations in biota reflect both chemical availability and bioaccumulation potential, both of which have direct toxicological significance (Williams *et al.*, 1994a; Wright & Mason, 1999).

Salt marshes (and contiguous shorelines) in Ireland and elsewhere are under threat from several anthropogenic sources, including organic pollutants, metals, engineering developments and agriculture (Beeftink *et al.*, 1982; Otte *et al.*, 1991; Fletcher *et al.*, 1994; Curtis & Sheehy Skeffington, 1998). Compared with many terrestrial ecosystems, the salt marsh flora is species-poor (Adam, 1990). However, this flora is uniquely adapted to frequent changes in salinity and flooding. Differential tolerance between species to tidal submergence and salinity produces a clear zonation from low to middle to upper marsh (Rozema *et al.*, 1985). The lower limits of halophyte distribution in salt marshes are determined by environmental physicochemical factors such as tolerance to salinity, flooding and tidal action, whereas the upper limits of plant distribution in areas of lower salinity and reduced flooding are determined by competition (Ungar, 1998). Along the lower marsh zone even small changes in elevation can make a critical difference in terms of tidal submergences (Zedler *et al.*, 1999) and thus favour one species over another.

Salt marshes act as sinks for anthropogenically derived metal contaminants. Salt marsh plants take up metals predominantly through the root system, with subsequent acropetal translocation from the root to the aerial parts (Rozema *et al.*, 1988). Monocotyledonous species tend to accumulate metals in the roots, whereas in dicotyledonous species, accumulation in the shoots is also significant (Otte *et al.*, 1991; Reboredo, 1993). Salt marsh plants have been used for biomonitoring purposes, although metal uptake is affected by a variety of factors including differences in age and growth stages, seasonal variations, presence of iron plaques on the roots, level of metal contamination in the locality, soil properties, tidal inundations, pH and salinity (Beeftink *et al.*,1982; Rozema *et al.*, 1990; Otte *et al.*, 1989, 1991, 1993; Williams *et al.*, 1994a; Sundby *et al.*, 1998; Caçador *et al.*, 2000).

There is normally a clear vertical and lateral zonation of seaweed species along an estuary, corresponding primarily to the salinity gradient but also to immersion/dessication cycles, competition and grazing (Raffaelli & Hawkins, 1996). The midlittoral zone is the main tidal belt along the vertical axis of the shore and it is dominated by brown seaweed species (Phaeophyta). Seaweeds integrate short-term temporal fluctuations in metal concentrations in water (Bryan & Hummerstone, 1973; Phillips, 1994), and brown seaweed species have been widely used for biomonitoring of metal contaminants in estuarine environments (Barnett & Ashcroft, 1985; Molloy & Hills, 1996; O'Leary & Breen, 1998; Stengel & Dring, 2000). Much less research has been done on the use of red seaweed species (Rhodophyta) for biomonitoring purposes, probably because of their relative scarcity compared with the brown seaweeds along the midlittoral zone.

Phillips (1977) cautioned against trying to correlate the concentrations of metals in seaweed tissue and seawater because of the extraneous effects of water sampling and environmental variables such as salinity, turbidity and water temperature. However, other researchers (Morris & Bale, 1975; Seeliger & Edwards, 1977) did find good agreement between concentrations of metals in water and *Fucus vesiculosus*. Leal *et al.*, (1997) recorded good correlations between mean metal concentrations in seawater and algae species from monthly samplings over an eight-month period.

Midlittoral sediments are probably the most widely used for monitoring metal concentrations in estuaries (Salomons, 1985; Bryan & Langston 1992; Harland *et al.*, 2000). The accumulation of metals in sediments is influenced by a complex host of physico-chemical and biogeochemical reactions, occurring both in the water column and at the sediment-water interface, as controlled by metal speciation, salinity, pH, redox potential and the presence of complexing agents

(Fletcher *et al.*, 1994). Comparisons have been made between metal accumulation in midlittoral sediments and vegetated salt marsh sediments, and higher metal concentrations have generally been found in the marsh sediments (Phillips, 1994; Wright & Mason, 1999). Several reasons have been posited for this, including different hydraulic regimes and higher organic matter content.

The primary aims of the research were:

1. To describe the lower salt marsh vegetation and midlittoral seaweed species of the Suir Estuary.

2. To compare metal concentrations in midlittoral sediments and salt marsh sediments in the Suir Estuary.

3. To investigate the concentrations of metals in salt marsh plant species and to examine factors that influence the use of salt marsh plant species for biomonitoring purposes.

4. To compare metal concentrations in three brown (Phaeophyta) and one red (Rhodophyta) seaweed species on the Suir Estuary and to compare species for biomonitoring purposes.

5. To make a set of recommendations for the management of metal pollution in the Suir Estuary.

The thesis consists of reports on four research projects, the aims of which are described above, and a General Discussion that includes recommendations. The research reports are presented in the format of scientific papers, one of which, (Chapter 6), has been accepted for publication by *Environmental Pollution*. Some minor repetition between chapters has been unavoidable due to the particular format used but this has been kept to a minimum.

# CHAPTER 2

# Background

**River Suir and main tributaries**

The River Suir[a] rises on the eastern slopes of Devil's Bit Mountain in Ireland, 150 kilometres from the sea, and is fed by numerous tributaries from mountains to the east and west (Figure 1). In its early stages, the River Suir flows due south toward the sea but is blocked by the Comeragh Mountains. The Suir takes a short loop northwards then eastwards along the base of the Comeragh Mountains until it circumvents this mountainous obstruction and finally heads for the sea through Waterford City[b]. Carboniferous limestone is the principal substratum for nearly the full course of the Suir River to the sea, and as a result the freshwater is alkaline with a mean pH of 8.2 (Bowman *et al.,* 1996).

The two main tributaries of the River Suir are the Barrow and the Nore, and both of these tributaries join the Suir in the lower part of the estuary, just 15 kilometres before the combined 'Three Sister' rivers flow out to the Atlantic Ocean. The River Nore rises on the north-eastern slopes of the Devil's Bit Mountain, very close to the origin of the River Suir (Figure 1). The River Barrow rises on the northern slopes of the Slieve Bloom Mountains and is joined by the River Nore north of New Ross town, before their combined waters flow into the lower Suir Estuary at Cheekpoint (Figure 2).

---

[a] The name Suir is derived from the Gaelic 'Súir' which means 'sister'.

[b] The name Waterford is derived from the Old Norse Vedra-fjordr which means 'ram fjord or windy fjord'. The modern Irish name, Port Lairge, is thought to commemorate Laraig, an early Viking leader. (Bradley & Halpin 1992).

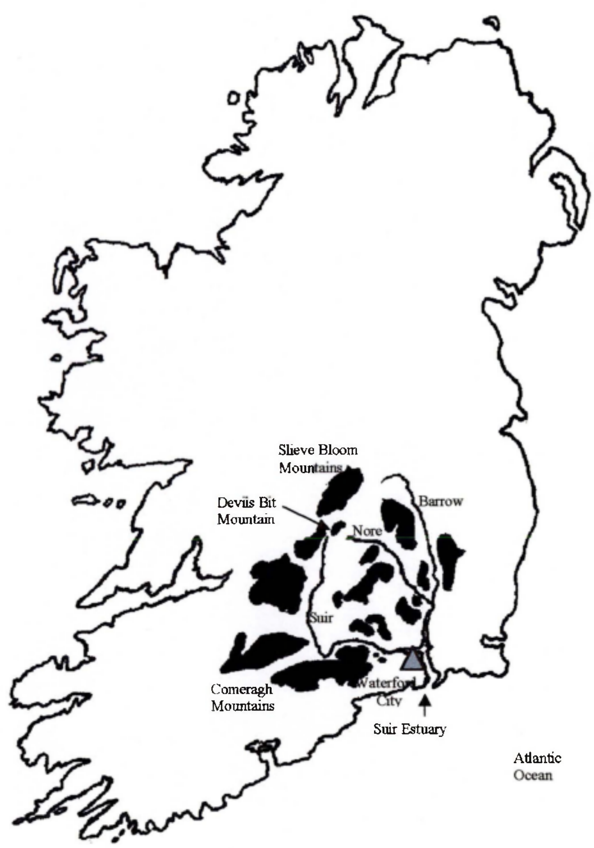



**Figure 1**. The River Suir and main tributaries

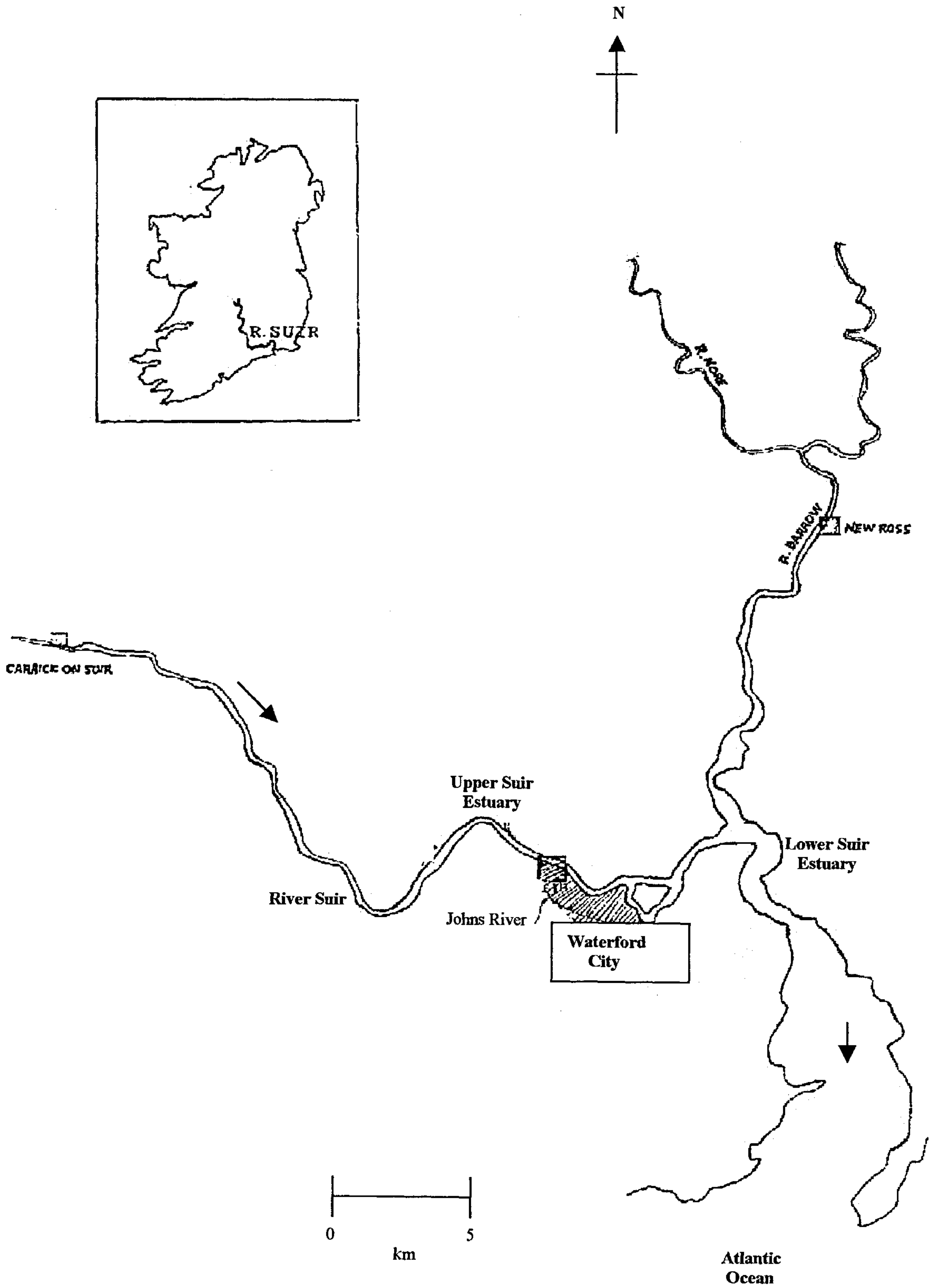



**Figure 2**. Suir Estuary and tributaries
Arrows indicate direction of flow

The 'Three Sister' rivers (Suir, Barrow, Nore) form the second largest river system in Ireland after the River Shannon (Table 1). The combined freshwater flows of all three rivers have carved out the Suir Estuary, that, since Viking times, has been an important harbour.

**Suir Estuary**

Cameron and Pritchard (1963) defined an estuary principally in terms of its physical structure :

> 'An estuary is a semi-enclosed coastal body of water which has free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage'

According to a classification system proposed by Pritchard (1967) the Suir Estuary can be described as a coastal plain estuary. In common with others of this type, the Suir Estuary was formed by the flooding of the river valley from the sea and it retains the characteristic V-shape. The tidal cycle in the Suir estuary is semi-diurnal i.e. two high tides per day. The high-low tidal cycle takes slightly over 6 hours. The mean spring tidal range is 3.6 metres and the mean neap tidal range is 2.2 metres at the mouth of the estuary. The contra-flowing tidal prism brings a large volume of saline water up the estuary to a maximum distance of 37 kilometres in the river Suir (spring tide/low freshwater flow). However, the tidal influence can extend to approximately 60 kilometres inland at spring tide (Neill, 1998).

**Table 1.** Suir-Barrow-Nore river and estuary system

| | | | |
|---|---|---|---|
| **Volumetric flows** ($m^3\ s^{-1}$) | | **Tidal prism** (million $m^3$) | |
| Suir | 63 | Spring tide | 280 |
| Barrow | 30 | Neap tide | 168 |
| Nore | 36 | | |
| | | **Salinity levels**[a] ($g\ l^{-1}$) | |
| **Catchment area** | | Estuary mouth | 38.5 |
| 9000 sq kilometers | | Passage East | 22.5 |
| | | Killoteran | 0.02 |

Source: Neill, 1998
[a]Recorded in December 1998 as part of this project

**Potential sources of metal pollution**

The River Suir and its tributaries flow through a region of relatively low industrial activity. There are a number of electronic, chemical, light engineering and food processing plants along the banks of the 'Three Sister' rivers. Waterford City and its immediate hinterland has a relatively high concentration of industrial activity compared to the rest of the south-east region of Ireland but this is low by industrial Britain or mainland Europe standards. The catchment area of the 'Three Sister' rivers, however, is in a region of major agricultural activity.

In May 1990 a report entitled *Water Quality Management Plan for the Suir Barrow Nore Estuary* was published which set out water quality standards for the estuary (Carlow County Council, *et al.*, 1990). Maximum allowable concentrations for a number of metals were included in the standards (Table 2).

**Table 2.** Maximum allowable concentrations in estuary water (mg $l^{-1}$) for a number of metals from the *Water Quality Management Plan for the Suir/Barrow/Nore Estuary 1990.*

| Metal | Standards (mg $l^{-1}$) | Comments |
|---|---|---|
| Copper | < 0.05 | General standard |
| Lead | < 0.10 | General standard |
| Chromium | < 0.05 | Mariculture areas |
| | < 0.10 | Elsewhere |

Source: Carlow County Council *et al.*, 1990.

Since 1990, major residential and industrial expansion has taken place in and around Waterford City. Part of this development is going on along the banks of the Suir Estuary and salt marsh areas are gradually being encroached upon. This trend makes the current project all the more important, to serve as a baseline for the monitoring of future developments.

Three metals were studied as part of this project and they each have a number of potential anthropogenic sources on the Suir Estuary or on the rivers flowing into it.

**Copper**

Copper is widely used in a variety of industrial, commercial, agricultural and domestic situations in the region, e.g. industrial boilers, plumbing, electrical wiring, household utensils, etc. Brass is an alloy of copper and zinc while bronze is an alloy of copper and tin. Significant quantities of organo-copper compounds are used as fungicides for control of crop diseases in the region, including blight (*Phytophthora infestans*) in potatoes and scab (*Venturia inequalis*) in apples.

**Lead**

There is a major glass crystal manufacturing plant in Waterford City that was set up in 1947. Lead oxide is used in the production of the heavy crystal pieces and this is a potential source of pollution into the estuary, *via* the Johns River tributary. Since March 1997 large consignments of zinc sulphide ore have been shipped from New Ross harbour out through the Suir Estuary. There is approximately 2 per cent content of lead sulphide in zinc ore and this makes it a potential source of lead pollution in the estuary. Lead piping is still in use in some of the older water supplies in Waterford City and in towns upstream, although it is gradually being replaced. Other sources of lead include batteries and scrap metal.

**Chromium**

Large volumes of chromium sulphate solutions were used for chrome-tanning in local leather tanneries and subsequently disposed of into the upper reaches of the Suir Estuary. A major plant at Portlaw on the Clodiagh River, a tributary of the Suir, closed in 1985 after operating for 51 years. It initially used the vegetabletanning process but switched to chrome-tanning about 1950. A smaller plant at Carrick-on-Suir, at the head of the estuary, closed in 1985 after 53 years in production. This plant used chromium sulphate from the outset. There were no pollution control measures in operation in these plants and it is likely that chromium residues will continue to have an impact on the Suir Estuary into the future. In 1993 a new tannery opened on the banks of the estuary, not far from the old plant at Portlaw. This plant also uses chromium sulphate but has pollution treatment measures in operation. Because of its hardness, chromium is widely used as an alloy with other metals, and makes up 10 percent or more of stainless steel. It is also used as a body trim on automobiles, and in household appliances.

**Study sites**

A total of ten sites were identified at the beginning of the project, in spring 1995. Two minor salt marsh sites, close to Waterford City, were lost to land development (infill) early in the project and are not included in the final results. The remaining eight sites are listed in Table 3 and locations shown in Figure 3. Surface estuary water and midlittoral sediment samples were analysed for Cu, Pb and Cr concentrations at all eight sites. Six of the sites contained salt marsh vegetation, and a detailed description of the lower salt marsh vegetation was recorded. The main plant species at these sites were analysed for metal concentrations. Midlittoral seaweed species were present at five of the sites. A detailed description of the species was made, and these were also analyzed for metals.

**Table 3.** Location of study sites on the Suir Estuary.

| site | coordinates* |
|---|---|
| Killoteran | S 544 106 |
| Granagh | S 587 142 |
| Johns River | S 614 124 |
| Maypark | S 635 118 |
| Belview | S 654 122 |
| Ballinakill | S 647 103 |
| Cheekpoint | S 683 137 |
| Passage East | S 701 103 |

* Ordnance Survey of Ireland: 1/50,000 Discovery Series, number 76

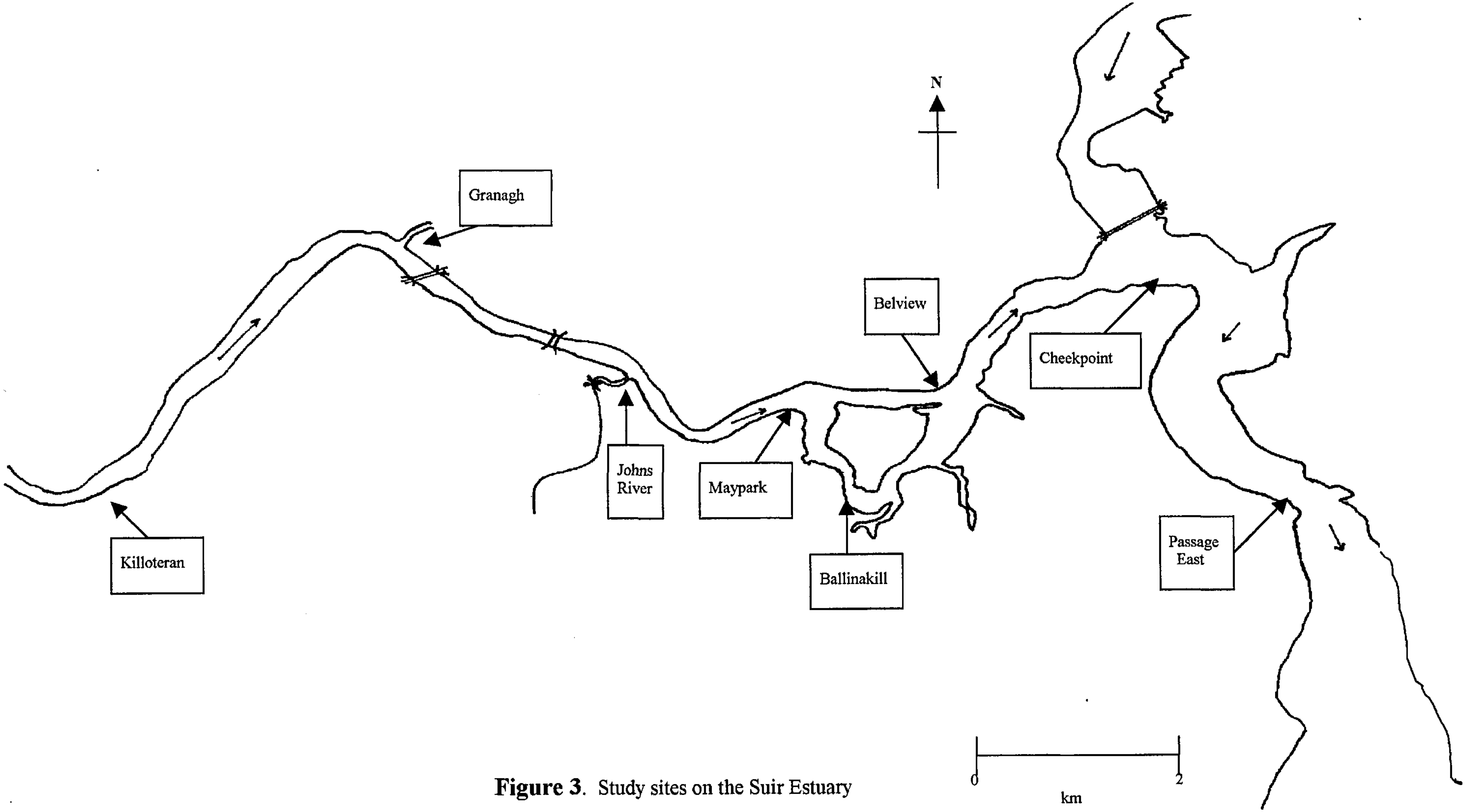



**Figure 3**. Study sites on the Suir Estuary

Arrows indicate direction of flow

# CHAPTER 3

# Material and Methods

## Introduction

Samples were taken from a number of compartments within the Suir Estuary during the course of this study and analyzed for Cu, Pb and Cr concentrations (Table 1).

**Table 1.** Location of sites on the Suir Estuary where midlittoral sediment, salt marsh vegetation, seaweed spp., and surface estuary water were sampled and analyzed for metal concentrations in 1997-1998.

| site | coordinates* | sediment | salt marsh vegetation | seaweed spp. | water |
|---|---|---|---|---|---|
| Killoteran | S 544 106 | + | + | | + |
| Granagh | S 587 142 | + | + | | + |
| Johns River | S 614 124 | + | | + | + |
| Maypark | S 635 118 | + | + | + | + |
| Belview | S 654 122 | + | + | + | + |
| Ballinakill | S 647 103 | + | + | | + |
| Cheekpoint | S 683 137 | + | + | + | + |
| Passage East | S 701 103 | + | | + | + |

+ samples collected for metal analysis

* Ordnance Survey of Ireland: 1/50,000 Discovery Series, number 76

## Analysis of estuary water

*Sampling of estuary water*

In December 1998, four 250 ml samples were taken from the surface of the water in high density polyethylene (HDPE) bottles, from the bank of the Suir Estuary, within one hour either side of high tide, at each of the three sites. HDPE bottles were used in order to minimize adsorption losses to the surface of the container (Allen, 1989; Cresser, 1994). Immediately on return to the laboratory, 25 ml sub-samples were filtered using Whatman 4 filter paper and placed in a fridge at 4°C for subsequent metal analysis.

The temperature and pH of the estuary water were recorded at each site at the time of sampling.

*Determination of salinity of estuary water*

Salinity measurements were taken at the laboratory using the argentometric titration method (APHA Standard Methods, 1992):

Reagents

(a) Potassium chromate indicator solution

50 g $K_2CrO_4$ was dissolved in distilled water. $AgNO_3$ was added until a red precipitate formed. This indicator solution was allowed to stand for 12 hours, filtered, and made up to 1 litre with deionised water.

(b) Standard silver nitrate titrant 0.0141*M*

2.39 g of $AgNO_3$ was dissolved in distilled water and made up to 1 litre. This $AgNO_3$ solution was standardized by titrating with standard NaCl using the $K_2CrO_4$ indicator solution.

(c) Standard sodium chloride 0.0141$M$

824 mg NaCl was dissolved in distilled water and made up to 1 litre.

Procedure

A 1.0 ml $K_2CrO_4$ indicator solution was added to 100 ml water samples. The samples were then titrated with standard $AgNO_3$ titrant to a straw coloured end-point. 1.0 ml $K_2CrO_4$ was also added to 100 ml samples of deionised water for use as blanks.

Calculations

$$\text{mg Cl}^- \text{ l}^{-1} = \frac{(A - B) \text{ x } M \text{ x } 35{,}450}{\text{ml sample}}$$

where: A = ml titration for sample

B = ml titration for blank

$M$ = molarity of $AgNO_3$

$$\text{mg NaCl l}^{-1} = (\text{mg Cl}^- \text{ l}^{-1}) \text{ x } 1.65$$

*Determination of Cu, Pb and Cr concentrations in estuary water*

The Varian SpectraAA 600 atomic absorption graphite furnace spectrophotometer (AAGFS) was used to analyse Cu, Pb and Cr concentrations. The accuracy of the AAGFS was confirmed using quality control samples of known metal concentrations. For Cu and Pb analysis, a pyrolytic graphite platform was added to the graphite tube to reduce matrix interference by the salt water ions. To further reduce matrix interference for Pb analysis in the higher salinity samples (>13 g $l^{-1}$), various chemical modifiers were tried. These included different concentrations of ethylenediaminetetra-acetic acid (EDTA) and ammonium pyrrolidine dithiocarbamate (APDC) using methyl isobutyl ketone (MIBK) as a solvent. However, matrix interference by salt ions still remained high and AAGFS readings for Pb concentrations were not reliable. Eventually a 2% w/v ammonium oxalate solution combined with APDC (Nham 1989) was successfully used as follows:

2 g ammonium oxalate was dissolved in 100 ml deionised water.

1.5 g APDC was dissolved in 100 ml deionised water and filtered through a Whatman 1 filter paper into a flask.

5 ml of the filtered APDC solution was added to the ammonium oxalate solution with 30 ml di-isobutylketone (DIBK) and shook vigorously for 3 minutes in a seperation funnel. The solution was left stand to allow for separation of the two phases. The lower aqueous phase was retained and the organic layer discarded. The extraction process was repeated twice more. The ammonium oxalate solution was then ready for use as a modifier.

The ammonium oxalate acted as a chelating agent with the majority of saltwater ions that were interfering with Pb analysis in the AAGFS.

No additional attachments or modifiers were required for Cr analysis.

**Analysis of Sediment porewater**

*Sampling of sediment porewater*

Sediment porewater salinity concentrations were recorded at each of the eight sites in 1998. A simplified version of a dialysis vial (Teasdale *et al.*, 1995) was devised to collect the sediment porewater. Porous nylon mesh (0.25 $mm^2$) was securely fastened over the tops of 250 ml wide-necked plastic (HDPE) containers. Four containers were inserted into the sediment at root level along the lower marsh zone at each site in November 1998. The first container was inserted at the furthest upstream point of the salt marsh and the remaining three were inserted at equal distances along the full length of the lower marsh zone. The containers were inserted in level locations in the lower marsh sediment but elevation above O.D. was not recorded for each container. Approximately 4 weeks after planting, the containers were retrieved and the contents decanted into clean 250 ml plastic bottles and brought back to the laboratory.

*Determination of salinity in sediment porewater*

Salinity measurements were recorded using the Argentometric titration method for chloride, as for estuary water (APHA Standard Methods, 1992).

**Analysis of seaweed material**

*Sampling and pretreatment of seaweed spp.*

Sampling of four seaweed species (*F. vesiculosus*, *F. serratus, A. nodosum* and *P. lanosa*) was carried out at the five sites on 14-16$^{th}$ December 1998. Four specimens of each species were collected at each site and mature parts of the thallus were cut from full-size specimens. In the case of *A. nodosum* the growing tips and new fronds including the first internode and first two vesicles were discarded. Lengths of thalli, approximately 20 cm long and including the second and subsequent internodes, were then harvested. In the case of *F. vesiculosus* and *F. serratus* the growing tips and first 3-5 cm of fronds were discarded and approximately 10 cm lengths of the remaining upper thalli were harvested. The mature thalli were then transported to the laboratory in plastic bags and frozen at $-10^{\circ}C$. After thawing, larger specimens of *P. lanosa*, approximately 10 cm in length, were removed from *A. nodosum* and thoroughly washed with deionised water. The fronds of *F. vesiculosus*, *F. serratus,* and *A. nodosum* were vigorously scrubbed with a nylon brush and deionised water. The samples of seaweed were dried at $80^{\circ}C$ for 24 h. and ground to powder using a mortar and pestle.

*Determination of Cu, Pb and Cr concentrations in seaweed spp.*

For metal analysis, 5 ml $HNO_3$ was added to 0.5 g of dry homogenized seaweed sample in a glass Kjeldahl flask fitted with a condenser and a water lock. The mixture was heated to approximately $100^{\circ}C$ until the formation of nitrous fumes ceased. Then the mixture was boiled until most liquid had evaporated. The remaining digest (approx. 1 ml) was diluted with deionised water to 20 ml, filtered using Whatman 4 filter paper, and stored in HDPE bottles. Blanks were prepared in the same way. All glassware was rinsed in dilute (7:1) nitric acid. Extracts were analysed for Cu, Pb and Cr using a Varian SpectraAA 600 flame spectrophotometer (AAFS). The accuracy of the AAGFS was confirmed using quality control samples of known metal concentrations.

**Analysis of salt marsh plant material**

*Sampling and pretreatment of salt marsh plant spp.*

Sampling of salt marsh plants was carried out at four sites in 1997 and six sites in 1998. In 1997 four plants of each species were collected from the lower salt marsh zone at each site. The roots and shoots were separated and placed in labelled plastic bags. The plant samples were then transported to the laboratory and frozen at $-10^0$C.

In 1998 four plants of each species were again collected from the lower salt marsh zone. This time only the roots <u>or</u> shoots of each species were retained for logistical reasons. The decision whether to collect roots or shoots was based on 1997 results. The plant segment (root or shoot) with the higher metal concentrations in 1997 was sampled in 1998. This was done to reduce the total number of samples for analysis.

*Determination of Cu, Pb and Cr concentrations in salt marsh plant spp.*

After thawing, the plants roots were washed with deionised water. Samples (approximately 5 g) were then dried at $80^0$C for 24 h. The roots were ground to powder using a mortar and pestle. Then 10 ml of $HNO_3/HClO_4$ (7:1 v/v) was added to 100 mg dry homogenized plant material in a Kjeldahl flask fitted with a condenser and water trap. The mixture was heated slowly to approx. $100^0$C until the formation of nitrous fumes stopped. The mixture was then boiled to approx. $200^0$C until most of the liquid was evaporated. The remaining digest (approx. 0.5 ml) was diluted with deionised water to 10 ml, filtered using Whatman 4 filter paper, and stored in HDPE bottles. Blanks were prepared in the same way.

Extracts were analysed for Cu, Pb and Cr using a Varian SpectraAA 600 AAFS. The accuracy of the AAGFS was confirmed using quality control samples of known metal concentrations.

**Analysis of midlittoral sediment**

*Sampling and pretreatment of midlittoral sediment*

Samples of sediment from the midlittoral zone were taken at four sites in 1997. Sediment samples from the midlittoral zone were taken again at the same four sites, plus four additional sites, on the Suir Estuary in 1998.

Four samples of sediment were taken from the midlittoral zone at each of the sites in 1997 and 1998. The top 2 cm of sediment was sampled using a plastic scoop. Each sample was taken at low tide, approximately midway along the midlittoral zone. The four sampling points were roughly equidistant from each other along the length of the midlittoral zone, which varied in length from 140 metres (Belview) to 250 metres (Cheekpoint). The samples were transported to the laboratory in plastic bags and frozen at $-10^{o}C$.

*Determination of Cu, Pb and Cr concentrations in midlittoral sediment*

After thawing, the sediment was dried at $80^{0}C$ for 24 hours. The sediment lumps were gently broken up with a mortar and pestle and brushed through a 63 μm sieve. 1 g of sediment was weighed into a Kjeldahl flask fitted with a condenser and water trap, and 10 ml $HNO_3/HCl$ (1:3 v/v) was added. The mixture was heated at $80^{0}C$ for 2 hours in a water bath. The mixture was then boiled briefly, avoiding evaporation to dryness. The remaining digest was filtered using a Whatman 4 filter paper. The residue was washed twice with 10 ml deionised water and the filtrates added to the filtered extract. The mixture was boiled again, evaporated to about 5 ml and diluted to 15 ml. The mixture was filtered again using Whatman 4 filter paper and stored in HDPE bottles. Blanks were prepared in the same way. Extracts were analysed for Cu, Pb and Cr using a Varian SpectraAA 600 AAFS. Quality control samples of known metal concentrations were included in the analysis to verify the accuracy of the AAFS.

*Fraction of sediment particles < 63 μm (f < 63 μm)*

The < 63 μm particle size was proposed as a standard grain fraction by Förstner & Salomons (1980) in order to normalise grain size effects. The mobility of metals generally decreases with increasing fractions of < 63 μm particle size due to adsorption of the metals to these particles. The f < 63 μm was determined by wet sieving 5 g of dry sediment over a 63 μm mesh Impact sieve.

*Loss on ignition (LOI)*

LOI was carried out to determine carbon content of the sediment samples. This was done by ashing 1 g dry sediment for 3 hours at $600^0$C.

**Analysis of salt marsh sediment**

*Sampling and pretreatment of salt marsh sediment*

In September-October 1997 samples of sediment were taken from between the roots of four plants of each of the salt marsh species at each of the sites. The plants were sampled roughly equidistant from each other along the length of the lower salt marsh zone. The samples were transported to the laboratory in plastic bags and frozen at $-10^{o}C$.

*Determination of Cu, Pb and Cr concentrations in salt marsh sediment*

Cu, Pb and Cr concentrations in salt marsh sediments were determined according to the method used for midlittoral sediments.

*Fraction of sediment particles < 63 µm (f < 63 µm)*

The f < 63 µm was determined according to the method used for midlittoral sediments.

*Loss on ignition (LOI)*

LOI was carried out according to the method used for midlittoral sediments.

**Limits of Detection**

The limits of detection of absorbance ($LOD_{absorb}$) for Cu, Pb and Cr were determined by using the formula proposed by Ingle & Crouch (1988) for the AAFS, and Butcher & Sneddon (1998) for the AAGFS:

$$LOD_{absorb} = \frac{3\,\sigma_B}{s}$$

where $\sigma_B$ is the standard deviation of the blank absorbance and s is the slope of the calibration curve (calibration sensitivity). The LOD for each of the metals (mg $kg^{-1}$ for AAFS; µg $l^{-1}$ for AAGFS) was then calculated from the mean concentrations of the blanks by using the formula adapted from the US Geological Survey (1979):

**AAFS** (seaweed, vegetation, sediment):

$$\text{metal conc. (mg kg}^{-1}\text{)} = \frac{\text{AA conc. (mg l}^{-1}\text{) x dilution vol of sample (ml)/1000}}{\text{weight of sample in kg}}$$

**AAGFS** (estuary water):

$$\text{metal conc. (}\mu\text{g l}^{-1}\text{)} = \text{AA conc. (}\mu\text{g l}^{-1}\text{)}$$

**Statistical analysis**

Two-way analysis of variance (ANOVA) was carried out to compare the concentrations of metals between and within different sites in the various compartments in the Suir Estuary (water, sediments, salt marsh plant spp. and seaweed spp.) using Axum data analysis computer software (MathSoft, 1996). The Tukey test was used to determine inter-site differences in metal concentrations (Fowler & Cohen, 1990). The one-tailed t-test was used to test significant differences between plant shoot and root concentrations of metals. The Pearson Product Moment Correlation Coefficient was used to compare the relative concentrations of metals between the different compartments. It was also used to compare soil properties (LOI and f < 63 μm) with soil metal concentrations.

# CHAPTER 4

## A description of the lower salt marsh vegetation and the midlittoral seaweed species on the Suir Estuary

## SUMMARY

In July-August 1995 and 1996, populations of plant species were recorded along the lower salt marsh zone at six sites on the Suir Estuary. Populations of seaweed species were also recorded at five sites along the midlittoral zone of the estuary. There was a clear lateral zonation of species along the lower salt marsh zone from the freshwater-saltwater interface at Killoteran to the furthest downstream site at Cheekpoint. *Aster tripolium* and *Elytrigia atherica* had the widest distribution throughout the lower marsh zone but *E. atherica* was recorded at slightly higher elevations. *Elytrigia* spp. are sensitive to tidal immersions of seawater but even very small differences in elevation are sufficient to alter the intertidal environment. As the mean salinity of the sediment porewater increased, there was an increase in elevation from mid-salinity to high salinity sites for several species, including halophytes like *Plantago maritima, Armeria maritima, Agrostis stolonifera* and *Spartina* spp.. Some differences in plant height between low salinity and high salinity sites were recorded for *A. tripolium* and *E. atherica,* although intra-site variation was large. *Fucus vesiculosus* was the seaweed species with the widest distribution along the midlittoral zone of the Suir Estuary. Large populations of the Phaeophyceae, *F. vesiculosus* and *Ascophyllum nodosum,* were recorded at the middle and higher salinity sites. Large populations of *Polysiphonia lanosa* (Rhodophyceae) were also recorded at these sites, attached primarily to the fronds of *A. nodosum* on which it is hemiparasitic. *Fucus serratus* was present only at the high salinity site at Passage East. In common with salt marshes elsewhere in Ireland, the Suir Estuary salt marshes

and contiguous shorelines are under threat, principally from land development, especially salt marsh infill. This study could act as a baseline in the face of ongoing anthropogenic developments.

## INTRODUCTION

Coastal salt marshes may be defined as areas vegetated by herbs, grasses or low shrubs, bordering saline water bodies (Adam, 1990). Salt marshes are subject to major environmental impacts, including tidal inundation, salinity, erosion, sedimentation, and accretion (Beeftink, 1985). Salt marshes in Ireland and elsewhere are also under threat from anthropogenic sources including organic pollutants, metals, land development and agriculture (Beeftink *et al.*, 1982; Otte *et al.*, 1991; Fletcher *et al.*, 1994; Curtis & Sheehy Skeffington, 1998). Differential tolerance between species to tidal submergence and salinity produces a clear zonation from low to middle to upper marsh (Rozema *et al.*, 1985). In general, the lower limits of halophyte distribution in salt marshes are determined by environmental physicochemical factors such as tolerance to salinity, flooding and tidal action, whereas the upper limits of plant distribution in areas of lower salinity and reduced flooding are determined by competition (Ungar, 1998).

Salt marsh vegetation is normally species-poor, usually decreasing to a small number of species along the lower marsh zone (Adam, 1990). Typically, in a salt marsh, it is elevation that defines the extent of tidal flooding and exposure of plants to salinity, although the vertical range of a species may shift due to microtopographical differences (Zedler *et al.*, 1999). As a general rule, tolerance of high salinity is achieved at the expense of growth rate (Adam, 1990). In nutrient culture studies it was shown that the growth rates of *Aster tripolium* and *Spartina anglica* were reduced with increased salinity (Rozema *et al.*, 1985, 1990).

The lateral distribution (downstream) of salt marsh plant species into sites with increasing salinity is related to the salt tolerance of the species (Wilson *et al.*, 1996). They also concluded, however, that the upstream distribution of plant species is not related to salinity but that competition between species can significantly affect the zonation pattern.

There is also vertical and lateral zonation of seaweed species in an estuary. Salinity is the primary factor that governs the distribution of seaweed species laterally along a sheltered shore (Lewis, 1964). The midlittoral zone is the main tidal belt along the vertical axis of the shore and is inundated by tides every day. This zone is dominated by Fucaceae and there is a succession of brown seaweed species along the estuary. Raffaelli & Hawkins (1996) described the succession of seaweed species along an estuary and concluded that the principal environmental factors influencing distribution were salinity gradient, immersion/dessication, competition and grazing.

The objective of this phase of the study was to describe the vegetation growing along the lower salt marsh zone of the Suir Estuary and to describe the distribution of seaweed species present along the midlittoral zone of this estuary. This study could act as a baseline in the face of ongoing anthropogenic developments, in particular, salt marsh infill and envirotoxicological effects of metal pollutants.

## MATERIALS AND METHODS

### Area of study

Six salt marsh sites were identified along the Suir Estuary (Table 1, Figure 1), extending from the freshwater-saltwater interface (FSI) at Killoteran downstream to Cheekpoint. Five midlittoral sites were identified along the Suir Estuary (Table 1, Figure 2), extending from the mouth of Johns River, a minor tributary that flows through Waterford City, to Passage East.

**Table 1.** Location of salt marsh vegetation and seaweed sites on the Suir Estuary.

| site | coordinates | |
|---|---|---|
| | saltmarsh vegetation | seaweed |
| Killoteran | S 544 106 | |
| Granagh | S 587 142 | |
| Johns River | | S 614 124 |
| Maypark | S 635 118 | S 635 118 |
| Belview | S 654 122 | S 654 122 |
| Ballinakill | S 647 103 | |
| Cheekpoint | S 683 137 | S 683 137 |
| Passage East | | S 701 103 |

* Ordnance Survey of Ireland: 1/50,000 Discovery Series, number 76

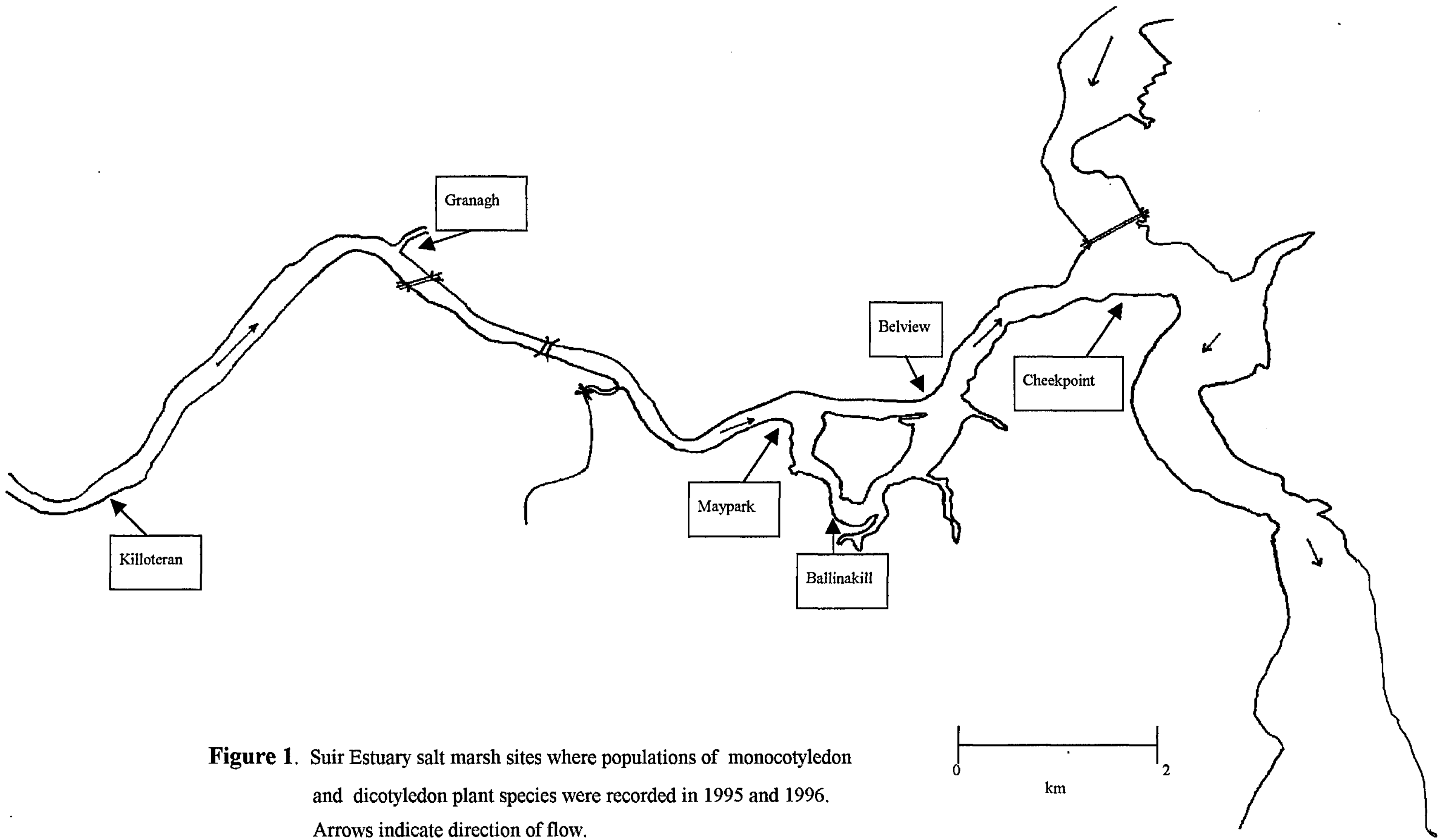



**Figure 1**. Suir Estuary salt marsh sites where populations of monocotyledon and dicotyledon plant species were recorded in 1995 and 1996. Arrows indicate direction of flow.

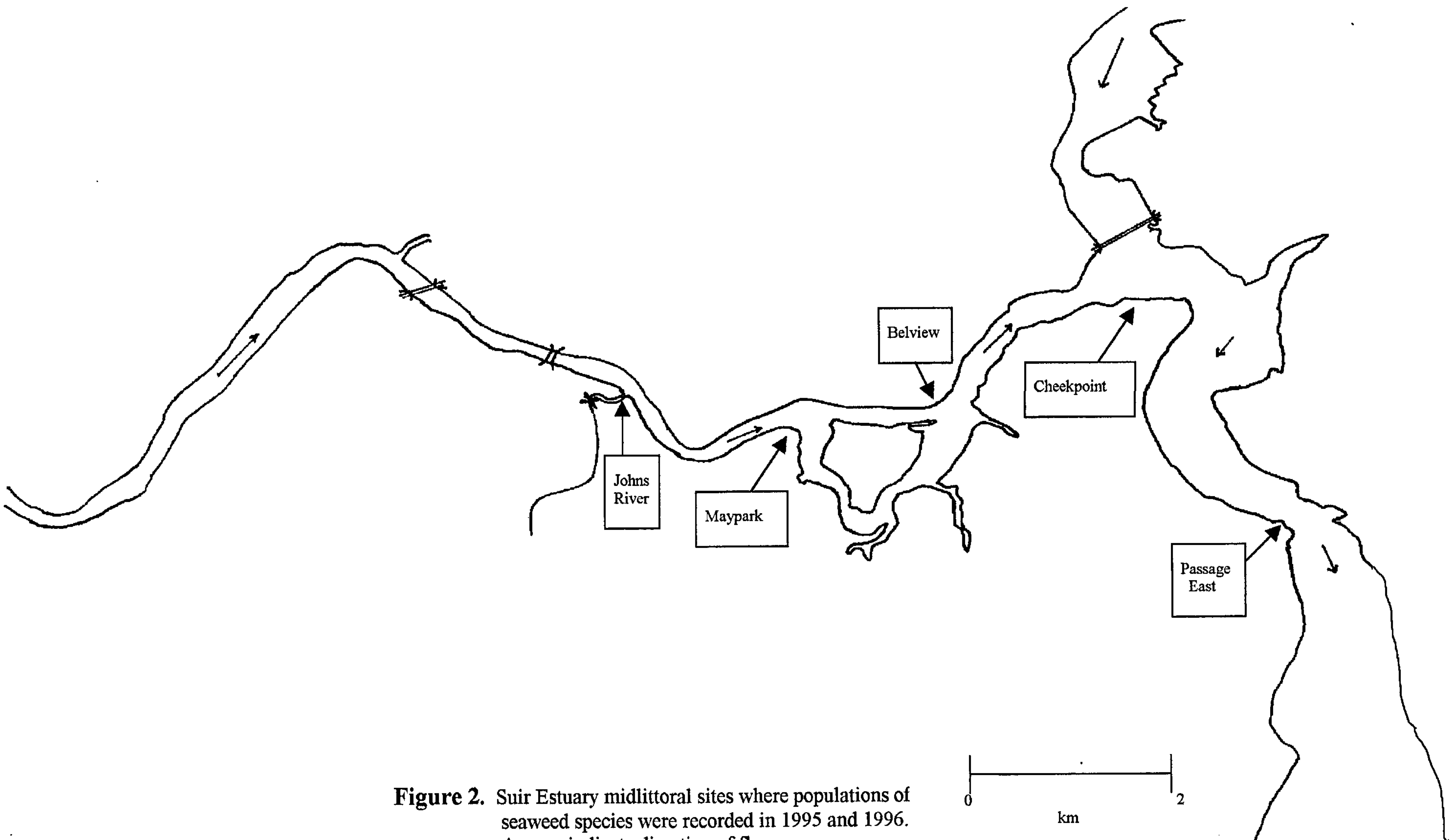



**Figure 2.** Suir Estuary midlittoral sites where populations of seaweed species were recorded in 1995 and 1996. Arrows indicate direction of flow.

**Salt marsh vegetation**

A 1-metre-wide parallel transect was established along the lower marsh zone at Ballinakill and Cheekpoint in July-August 1995 and at Killoteran, Granagh, Maypark and Belview in July-August 1996. The transect lengths corresponded to the lateral width of each lower marsh zone and were as follows: Killoteran, 160 metres; Granagh, 130 metres; Maypark, 420 metres; Belview, 150 metres; Ballinakill, 310 metres; and Cheekpoint, 260 metres. Percentage ground cover for each species was recorded using a 1 sq. metre quadrat at 10-metre intervals along the transects. Plant specimens were lodged with the Herbarium, National Botanic Gardens, Dublin, and identification confirmed (M. Jebb, personal communication).

Elevation above ordnance datum (O.D.) was measured by extending a 1.5 metre wooden pole, with attached levelling device, from each quadrat over the water level. The distance from the pole to the water level was then recorded using a tape measure. This was carried out at each site within a period of one hour either side of high tide. Elevation above O.D. for each quadrat was then calculated with reference to Tide Tables for the Port of Waterford. The mean height of each plant species, from soil level to the tip of inflorescence, was recorded at each quadrat and each species was described as either **vegetative** or **inflorescence** depending on the stage of growth.

**Seaweed populations**

A 0.25 metre-wide parallel transect was established mid-way along the midlittoral zone, where seaweed species were present, at Cheekpoint in September 1995, and at Belview and Passage East in October 1996. Only small, isolated populations of seaweed were recorded at Johns River and Maypark in 1996. The transect lengths corresponded to the lateral width of each midlittoral zone and were as follows: Cheekpoint, 250 metres; Belview, 140 metres; and Passage East, 70 metres. A 0.25 sq metre quadrat was located at 10 metre intervals along the transects and the number of holdfasts recorded for each species. The mean lengths of thalli were recorded for all species in each quadrat. In the case of *P. lanosa*, which is hemiparasitic (primarily on *A. nodosum*), a count was made of the total number of individuals attached to the host fronds in each quadrat.

# RESULTS

**Salt marsh vegetation**

The percentage ground cover of lower salt marsh plant species was recorded at six sites along the Suir Estuary during July-August 1995 and 1996 (Table 2). There was a succession of species along the lower salt marsh zone from zero sediment porewater salinity at Killoteran to the highest salinity site at Cheekpoint. Certain species were present only at zero salinity (e.g. *Apium graveolens, Calystegia sepium* and *Anthriscus sylvestris)*. Other species had a substantive presence across a wide salinity range on the estuary, e.g. *Aster tripolium* and *Elytrigia atherica.* Large populations of *Phragmites australis* and

**Table 2.** Mean percentage ground cover of plant populations measured at six lower salt marsh sites on the Suir Estuary during July-Aug 1995 and 1996. Sediment porewater salinity (g $l^{-1}$) recorded at each site in December 1998 is also presented.

| species | Killoteran | Granagh | Maypark | Belview | Ballinakill | Cheekpoint |
|---|---|---|---|---|---|---|
| *Apium graveolens* | 43 | | | | | |
| *Calystegia sepium* | 31 | | | | | |
| *Anthriscus sylvestris* | 4 | | | | | |
| *Phragmites australis* | 63 | 66 | | | | |
| *Schoenoplectus tabernaemontani* | | 40 | 13 | | | |
| *Aster tripolium* | | 17 | 24 | 9 | 18 | 9 |
| *Elytrigia atherica* | | 5 | 8 | 63 | 7 | 23 |
| *Atriplex prostrata* | | 0.1 | 2 | 1 | 7 | 0.1 |
| *Agrostis stolonifera* | | | 30 | 2 | 74 | 12 |
| *Spartina* spp. | | | 7 | < 0.1 | 1 | 10 |
| *Plantago maritima* | | | 7 | 6 | | 14 |
| *Juncus gerardii* | | | 6 | 7 | | |
| *Triglochin maritima* | | | 5 | 4 | 0.1 | 1 |
| *Festuca ovina* | | | 3 | | 8 | |
| *Armeria maritima* | | | 0.5 | 1 | | 4 |
| *Glaux maritima* | | | 0.5 | 2 | | |
| *Spergularia media* | | | | 0.1 | | 4 |
| *Limonium humile* | | | | | | 4 |
| Number of quadrats | 16 | 13 | 42 | 15 | 31 | 26 |
| Sediment porewater salinity (g $l^{-1}$) | 0 | 1.8 | 6.9 | 10.4 | 12.1 | 13.9 |

*Schoenoplectus tabernaemontani* were recorded at the lower salinity sites while *Plantago maritima* and *Agrostis stolonifera* were present in significant numbers at the mid- and high salinity sites.

On the Suir Estuary the sterile form of *Spartina*, *S.* x *townsendii*, was found at the Belview and Cheekpoint sites. The fertile form, *S. anglica*, was found at Maypark while both amphidiploid and polyhaploid forms of *Spartina* were found at the Ballinakill site. For the sake of clarity they are all referred to as *Spartina* spp. in this study.

Despite high intra-site variation there were appreciable differences in elevation between low salinity and high salinity sites for several species, including *P. maritima, A. maritima, E. atherica, A. stolonifera* and *Spartina* spp. (Table 3, Figure 3). The mean sediment porewater salinity and mean elevation above O.D. for all sites were calculated for each plant species (Table 4). The number of tidal floodings was calculated for each plant species from the mean elevation of each species above O.D. and from tide tables for the Port of Waterford for 1996. *Phragmites australis* was flooded nearly twice as often as *L. humile,* the species with the highest mean elevation. The relationship between the % ground cover of the main plant species and sediment porewater salinity and elevation above O.D. is shown in Figure 4. While *A. tripolium, A. stolonifera* and *E. atherica* have a widespread distribution across a range of salinities, there was a trend toward increased elevation as salinity increases. Product Moment Correlation analysis showed significant correlation between the % ground cover and sediment porewater salinity for a number of monocotyledonous species, including *P. australis, E. atherica* and *A. stolonifera* (Table 5). Only one species, *A. tripolium,* showed a significant correlation ($P < 0.01$) between % ground cover and elevation above O.D.

**Table 3**. Mean elevation (cm above O.D.) at each site for the main plant species. Sediment porewater salinity (g $l^{-1}$) measured at each site in December 1998 is also presented.

| species | Killoteran | Granagh | Maypark | Belview | Ballinakill | Cheekpoint |
|---|---|---|---|---|---|---|
| *Phragmites australis* | 352.0 (7.9) | 365.6 (20.1) | | | | |
| *Schoenoplectus tabernaemontani* | | 365.6 (20.1) | 360.7 (11.3) | | | |
| *Aster tripolium* | | 376.2 (34.7) | 366.6 (12.1) | 384.9 (12.8) | 389.2 (16.7) | 417.3 (12.1) |
| *Elytrigia atherica* | | 374.0 (24.3) | 367.5 (14.4) | 392.0 (8.3) | 397.2 (22.1) | 430.8 (8.8) |
| *Agrostis stolonifera* | | | 366.6 (12.1) | 387.2 (13.9) | 386.8 (15.5) | 419.7 (13.9) |
| *Spartina* spp. | | | 368.3 (12.8) | | 370.1 (0.9) | 411.3 (9.8) |
| *Plantago maritima* | | | 366.6 (12.1) | 387.2 (13.9) | | 419.7 (13.9) |
| *Armeria maritima* | | | 363.1 (2.9) | 376.4 (19.9) | | 425.5 (9.6) |
| *Limonium humile* | | | | | | 419.6 (8.1) |
| Sediment porewater salinity (g $l^{-1}$) | 0 | 1.8 | 6.9 | 10.4 | 12.1 | 13.9 |

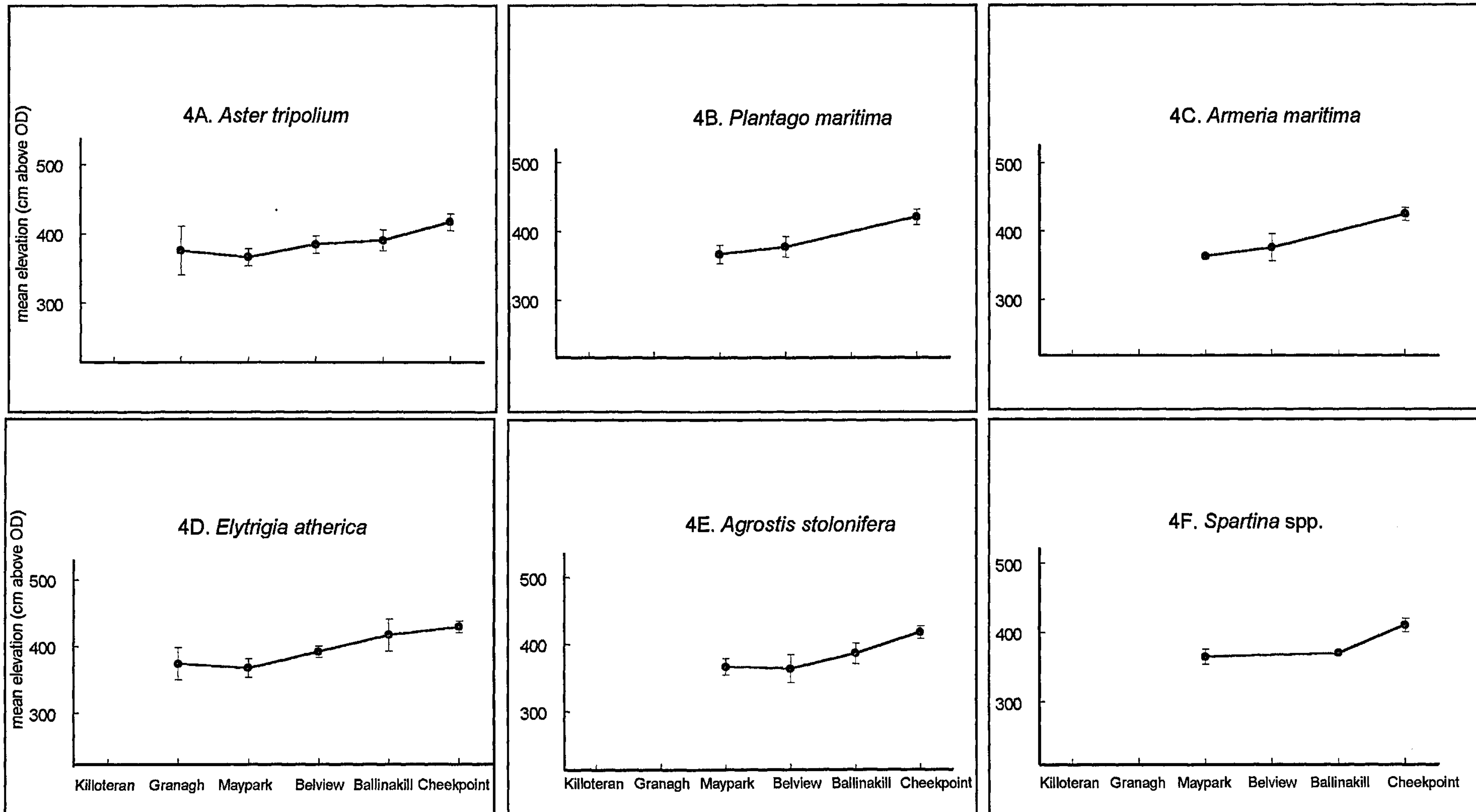



**Figure 3.** Mean elevation (cm above OD) at each site for six plant species. Vertical bars indicate standard deviation.

**Table 4.** Mean sediment porewater salinity (g $l^{-1}$), mean elevation (cm above O.D.) and number of floodings for all sites during 1996 for the main plant species.

| species | number quadrats | mean salinity (g $l^{-1}$) | mean elevation (cm above O.D.) | number floodings (1996) |
|---|---|---|---|---|
| *Phragmites australis* | 25 | 0.6 | 358.1 | 660 |
| *Schoenoplectus tabernaemontani* | 14 | 5.1 | 363.6 | 624 |
| *Spartina* spp. | 37 | 9.6 | 380.4 | 528 |
| *Aster tripolium* | 93 | 9.8 | 384.2 | 528 |
| *Elytrigia atherica* | 41 | 9.8 | 401.0 | 420 |
| *Agrostis stolonifera* | 87 | 10.0 | 382.2 | 528 |
| *Plantago maritima* | 35 | 10.3 | 390.7 | 480 |
| *Armeria maritima* | 16 | 11.7 | 401.5 | 420 |
| *Limonium humile* | 6 | 13.9 | 416.8 | 336 |

Total number of high tides in 1996 = 720 (height range: 330 – 480 cm above O.D.)

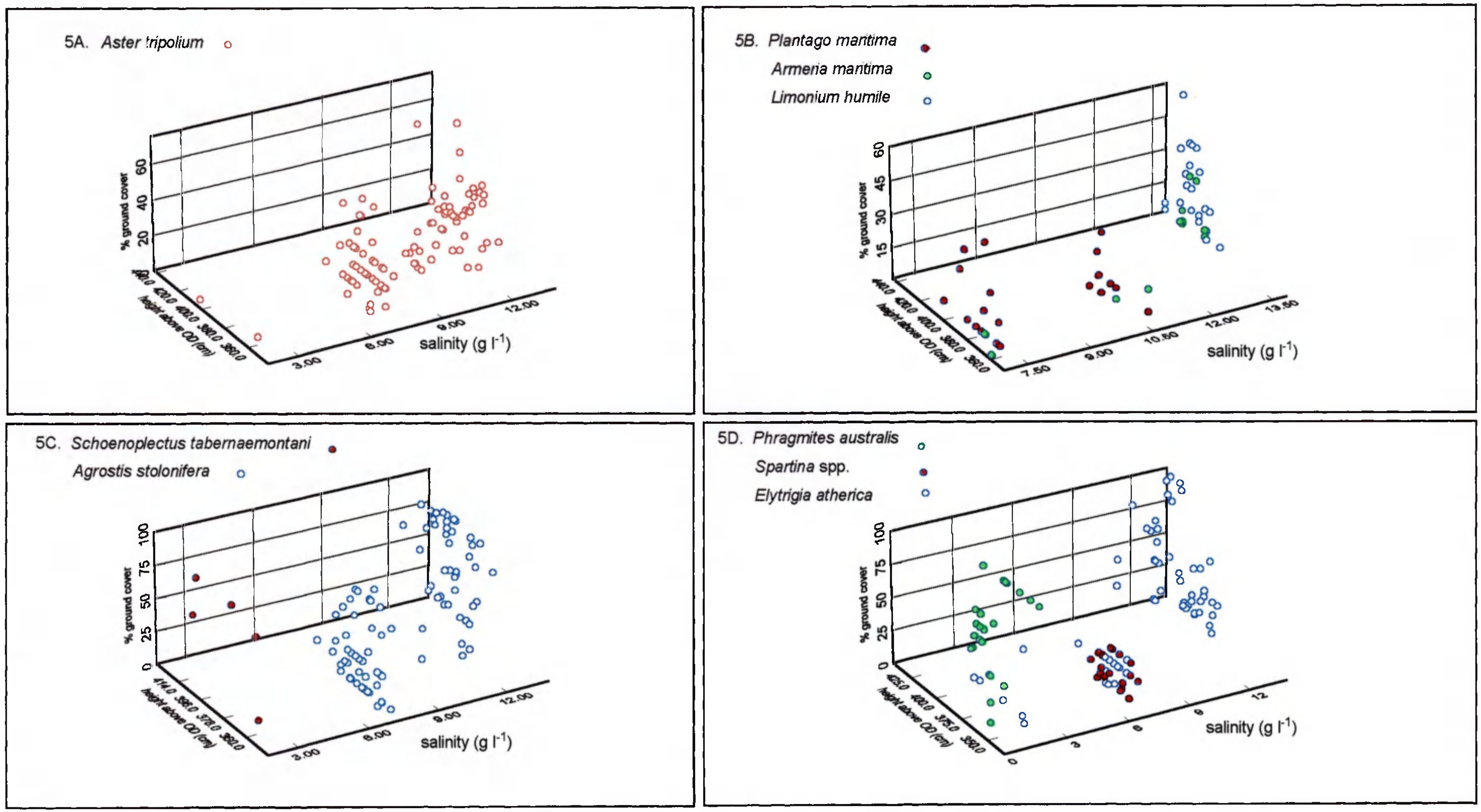



**Figure 4.** Relationship between % ground cover and elevation above OD (cm) and sediment porewater salinity (g l$^{-1}$) for various plant species

**Table 5.** Product Moment Correlation Coefficients (r) for % ground cover of several salt marsh plant species in 1995 and 1996 with sediment porewater salinity (g $l^{-1}$), and with elevation above O.D. (cm). n = number of sites (4 replications per site).

| species | | salinity / % ground cover | elevation above OD/ % ground cover |
|---|---|---|---|
| **Dicotyledons** | n | | |
| *Aster tripolium* | 5 | 0.17 | 0.30** |
| *Plantago maritima* | 3 | 0.10 | 0.20 |
| *Armeria maritima* | 3 | 0.10 | 0.00 |
| *Limonium humile* | 1 | - | 0.32 |
| **Monocotyledons** | n | | |
| *Phragmites australis* | 2 | 0.63** | 0.25 |
| *Schoenoplectus tabernaemontani* | 2 | 0.20 | 0.22 |
| *Spartina* spp. | 3 | 0.14 | 0.00 |
| *Agrostis stolonifera* | 3 | 0.30** | 0.00 |
| *Elytrigia atherica* | 5 | 0.36* | 0.22 |

* $P < 0.05$, ** $P < 0.01$

The mean height of the plant species at each site was measured and is summarised in Table 6. Most species were at the inflorescence stage except the monocotyledons, *P. australis, A. stolonifera* and *Spartina* spp., which were still at the vegetative stage in July-August. The intra-site variation was high, although there were height differences between low and high salinity sites in the case of *A. tripolium* and *E. atherica* (Figure 5).

**Table 6**. Mean height (cm) of the main plant species recorded in July-August 1995 and 1996. Standard deviations are shown in brackets.

| | **Killoteran** | **Granagh** | **Maypark** | **Belview** | **Ballinakill** | **Cheekpoint** |
|---|---|---|---|---|---|---|
| *Phragmites australis* (V) | 249 (10) | 243 (32) | | | | |
| *Sch. tabernaemontani* (F) | | 111 (9) | 95 (13) | | | |
| *Aster tripolium* (F) | | 110 (0) | 63 (17) | 59 (9) | 75 (14) | 38 (9) |
| *Elytrigia atherica* (F) | | 145 (0) | 89 (11) | 118 (5) | 94 (16) | 84 (22) |
| *Agrostis stolonifera* (V) | | | 61 (22) | 55 (0) | 80 (19) | 42 (11) |
| *Spartina* spp. (V) | | | 51 (11) | | 115 (0) | 47 (5) |
| *Plantago maritima* (F) | | | 40 (10) | 43 (4) | | 32 (4) |
| *Armeria maritima* (F) | | | 31 (5) | 31 (13) | | 23 (7) |
| *Limonium humile* (F) | | | | | | 30 (11) |
| no. of quadrats | 16 | 13 | 42 | 15 | 31 | 26 |

V = vegetative growth F = inflorescence

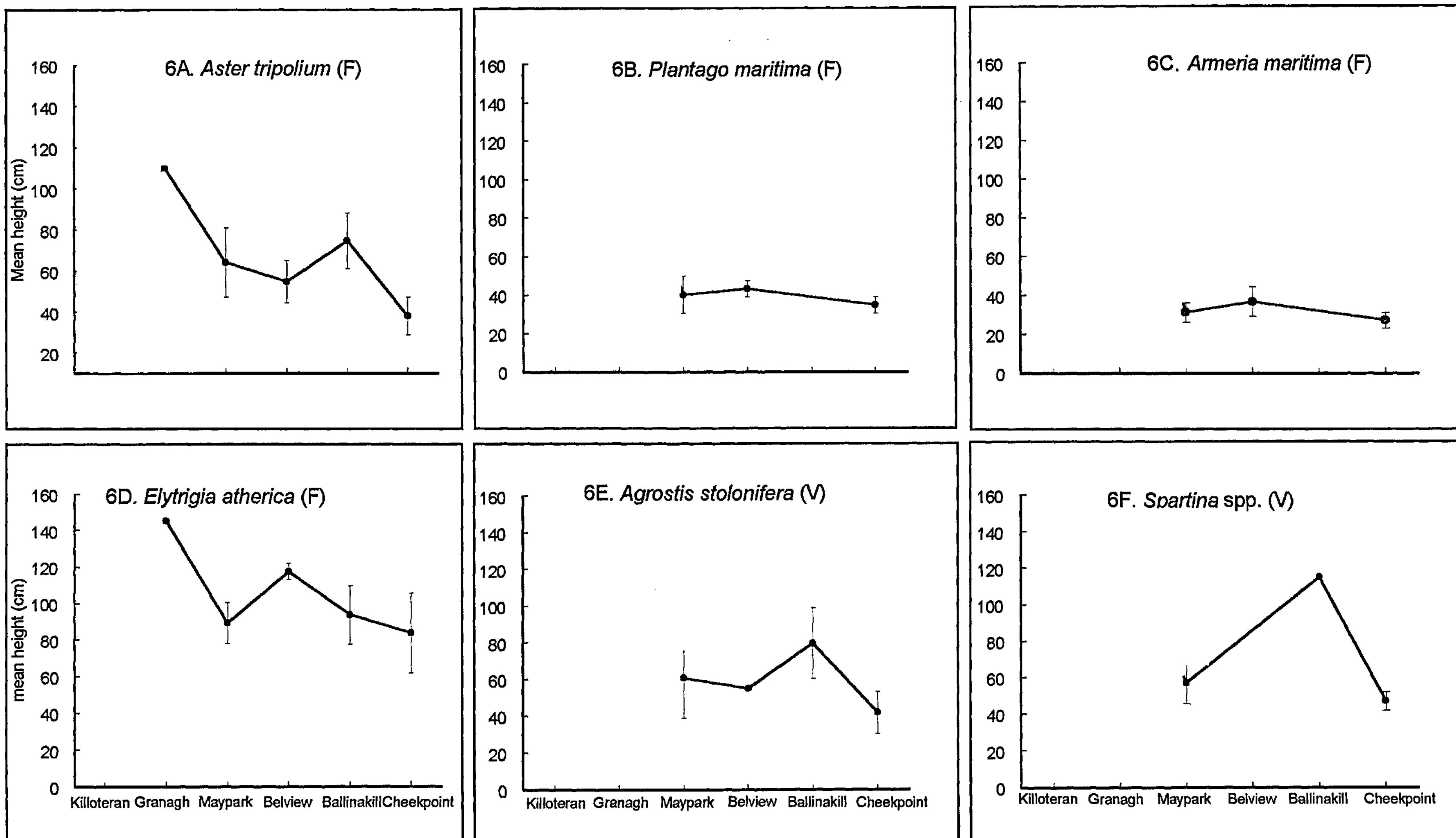



**Figure 5.** Mean height (cm) of six plant species measured in July-August. Vertical bars indicate standard deviation.

V = vegetative growth F = inflorescence

**Seaweeds**

Small isolated colonies of *F. vesiculosus, A. nodosum* and *P. lanosa* were present at the upstream site at Maypark but only *F. vesiculosus* was recorded at Johns River (Table 7). Further downstream there were substantial populations of these species, including very dense colonies of the epiphyte *P. lanosa* attached to the fronds of *A. nodosum* at Cheekpoint and Passage East. Occasionally, smaller sized specimens of *P. lanosa* were also found attached to *F. vesiculosus*. There were large populations of *F. serratus* at Passage East.

**Table 7.** Mean populations of seaweed spp. (number of holdfasts per 0.25 $m^2$ quadrat) measured midway along the midlittoral zone at five sites on the Suir Estuary during September- October 1995 and 1996. Mean surface water salinity (g $l^{-1}$) measured at each site in December 1998 is also presented.

| seaweed species | Johns River | Maypark | Belview | Cheekpoint | Passage East |
|---|---|---|---|---|---|
| *Fucus vesiculosus* | < 1 | < 1 | 22 | 29 | 25 |
| *Ascophyllum nodosum* | - | < 1 | 19 | 35 | 28 |
| *Polysiphonia lanosa*[a] | - | < 1 | 34 | 349 | 279 |
| *Fucus serratus* | - | - | - | - | 30 |
| n = number of quadrats per site | n/a | n/a | n = 15 | n = 26 | n = 8 |
| water salinity (g $l^{-1}$) (n = 4) | 17.3 | 13.0 | 15.6 | 17.7 | 22.5 |

n/a = not applicable. - not present

[a]hemiparasitic on *Ascophyllum nodosum*

# DISCUSSION

**Salt marsh vegetation**

The establishment and survival of plant species along the lower salt marsh zone is influenced principally by their ability to tolerate tidal submergences and differential resistance to salinity at the lower elevations of their range across the zone (Rozema *et al.*, 1985; Adam, 1990; Ungar, 1998). There was a clear lateral zonation of species along the lower salt marsh zone of the Suir Estuary, from the freshwater-saltwater interface (FSI) at Killoteran to the furthest downstream site at Cheekpoint. *Calystegia sepium* and *A. sylvestris* grow only in non-brackish sites (Webb, 1967) and were not recorded downstream of the FSI. Although *Apium graveolens* does grow in brackish sites (Webb, 1967), in this study it was observed only at Killoteran. *Phragmites australis* and *S. tabernaemontani* were abundant at the low saline sites and coexisted at low elevations where the roots were immersed almost twice daily during 1996. *Aster tripolium* and *E. atherica* had the widest distribution throughout the lower marsh zone of the Suir Estuary but *E. atherica* was growing at slightly higher elevations. *Elytrigia* spp. are sensitive to tidal immersions of seawater (Beeftink, 1985; Rozema *et al.*, 1985), but even very small differences in elevation are sufficient to alter the intertidal environment (Zedler *et al.*, 1999).

A number of species, including *Juncus gerardii, Triglochin maritima, Festuca ovina* and *Glaux maritima*, were present at mid-salinity sites but either decreased in density or were absent altogether at the high salinity site at Cheekpoint (Table 3). As the sediment porewater salinity increased, from mid-salinity to high salinity sites, there was an increase in the elevation of plant species. Elevation reduced exposure to flooding from increasingly saline water. These results are in agreement with Beeftink (1985) who found, with the same species, that as salinity increased, flood tolerance decreased.

Some differences in plant height between low salinity and high salinity sites were recorded for *A. tripolium* and *E. atherica,* although intra-site variation was large. Rozema *et al* (1985) recorded a significant reduction in growth in *A. tripolium* under saline conditions and also recorded reduced growth of *Spartina anglica* under increased concentrations of NaCl. They concluded that seawater salinity is the 'master factor' governing salt marsh zonation and succession and that flooding can be regarded as operating in addition to salinity effects.

**Seaweeds**

The number of seaweed species declines along an estuary in inverse proportion to salinity, although the relative abundance of individual species are not strongly correlated with salinity (Lobban & Harrison, 1997). Apart from the salinity gradient, which appears to be the primary factor influencing seaweed succession, other factors include immersion/dessication, competition and grazing (Raffaelli & Hawkins, 1996). The pH of the surface water of the Suir Estuary in December 1998 was remarkably similar for all sites.

*Fucus vesiculosus* was the seaweed species with the widest distribution along the midlittoral zone of the Suir Estuary in this study, although only small, isolated colonies were found at the two upstream sites, Johns River and Maypark. The relatively high salinity level recorded at Johns River, soon after high tide, was probably due to the much lower freshwater dilution capacity of this tributary compared to the River Suir.

Large seaweed populations were recorded at the three downstream sites - Belview, Cheekpoint and Passage East. Competition between fucoid species for space and light is an important determinant of distribution and this contributes to the mosaic of seaweed communities along an estuary. *Fucus vesiculosus* and *F. serratus* have a faster growth rate than *A. nodosum* and this gives them an advantage in the early stages of establishment (Raffaelli & Hawkins, 1996). However, *A. nodosum* is more tolerant of shady conditions than the *Fucus* species and this, combined with the longevity of individual plants (15 - 25 years), gives this species the advantage. *Ascophyllum nodosum* has an additional defence weapon in its armoury; compared to *Fucus* germlings, *A. nodosum* is relatively unpalatable to littorinid snails (Schonbeck & Norton, 1980). Nevertheless, in this study, *F. vesiculosus* and *F. serratus* competed well against *A. nodosum* along the midlittoral zone of the Suir Estuary, as confirmed by relative population densities at each of the sites.

A notable feature of *A. nodosum* populations on the Suir Estuary was the presence of *P. lanosa*, a red (Rhodophyta) seaweed, attached to the fronds. The populations of *P. lanosa* were dense at the two downstream sites, Cheekpoint and Passage East. *Polysiphonia lanosa* grows almost exclusively on *A. nodosum* but it has been reported on *Fucus* species (Dixon & Irvine, 1977; Garbary *et al.*, 1991). In this study, *P. lanosa* was occasionally found attached to *F. vesiculosus*, but only in a stunted form. In the past, *P. lanosa* was considered to be an epiphyte, principally because the amount of nutrient it received from the host, *A. nodosum*, was believed to be minimal (Fralick & Mathieson, 1975; Turner & Evans, 1977; Levin & Mathieson, 1991). More recent research has indicated however, that the relationship between *P. lanosa* and *A. nodosum* is more of a parasitic, or hemiparasitic, type (Penot *et al*, 1993; Ciciotte & Thomas, 1997).

Though the diversity of biota in the Suir Estuary salt marsh sites may be low compared to many terrestrial and marine ecosystems, nevertheless they are home to large populations of salt marsh plants and seaweed species, not to mention associated fauna. The main threat to the Suir Estuary is from land development, especially salt marsh infill, associated with urban sprawl (Waterford City). Since the commencement of this study in 1995, two small salt marsh sites, out of a total of eight, have been lost to development. Part of another site is to make way for a major roadway.

# CHAPTER 5

# Metal concentrations in midlittoral sediments and salt marsh sediments in the Suir Estuary

## SUMMARY

The concentrations of three metals, Cu, Pb and Cr, were recorded in midlittoral sediments along the Suir Estuary in 1997 and 1998, and in lower salt marsh sediments in 1997. Pb concentrations (range 14.7 – 63.4 mg $kg^{-1}$) and Cr concentrations (range 14.1 – 42.8 mg $kg^{-1}$) were particularly high in midlittoral sediments in the upper estuary, both probably due to substantial pollution inflows, current and historic. The deposition pattern for the three metals in the midlittoral sediments was similar for 1997 and 1998, and these, in turn, were very similar to metal concentrations recorded in the lower salt marsh sediments in 1997. The close correlation between metal concentrations in midlittoral sediments and lower salt marsh sediments taken from between the roots of *Aster tripolium* was probably linked to the similar organic matter contents in both sediment types. There was a high degree of correlation between Cu concentrations and organic matter in the mudflat sediments and salt marsh sediments.


## INTRODUCTION

Metals enter estuaries from feeder rivers and from direct discharges, and tend to accumulate in the sediments. The process of accumulation is influenced by parent material composition, particle size content, salinity, pH, redox potential, metal speciation, frequency of flooding, type and extent of vegetation in salt marshes, and other physico-chemical and biogeochemical factors (Beeftink *et al.*, 1982;

Williams *et al.*, 1994a; Fletcher *et al.*, 1994; Wright & Otte, 1999). Organic matter content is another key factor that affects the ability of sediments to retain metal ions *via* adsorption, chelation and ion exchange mechanisms (Elliott *et al.*, 1986; Otte *et al.*, 1991, 1993; Williams *et al.*, 1994b; Harland *et al.*, 2000). In general, the concentration of metals in sediments is higher in the upper parts of estuaries (Attrill & Thomes, 1995; Zwolsman *et al.*, 1996, Wright & Mason, 1999). This may be as a result of local anthropogenic sources in the upper estuary, the release of metals to the water column in the freshwater-saltwater interface, or the dilution of contaminated sediments by relatively clean marine sediments in the lower estuary.

Although sediments play a role in the removal of metals from the water column, there is the ongoing likelihood of remobilisation. Metals can be remobilised by physical disturbance from tidal action, storms and bioturbation (Fletcher *et al.*, 1994). Sediment-associated pollutants are less mobile than metals in solution and thus have a reduced toxicological significance. However, bacterial action, macrobenthos activity and sediment mixing can radically alter the metal speciation profile within aquatic sediments, and in some cases enhance toxicity to aquatic biota (Bubb & Lester, 1991). Metal accumulation is often greater in vegetated salt marshes than in midlittoral sediments (Fletcher *et al.*, 1994; Wright & Mason, 1999). Several reasons have been proposed for this including different hydraulic regimes and organic matter content.

The aims and expected outcomes of this study were:

(a) To determine if there was a difference in Cu, Pb and Cr concentrations in midlittoral sediments between the upper and lower Suir Estuary in 1998. It was expected that higher metal concentrations would be recorded in the upper estuary due to the concentration of industrial and residential developments there.

(b) To determine if there was a difference in Cu, Pb and Cr concentrations in midlittoral sediments throughout the Suir Estuary between 1997 and 1998. No differences in metal concentrations between 1997 and 1998 were expected because the sediment metal accumulation process is normally a gradual one in an estuary, except where major pollution events occur.

(c) To determine if there were differences in Cu, Pb and Cr concentrations between midlittoral sediments and lower salt marsh sediments, on the Suir Estuary in 1997. Differences were expected in metal concentrations between the two sediment types due to the presence of vegetation and associated organic material on salt marshes.

# MATERIALS AND METHODS

## Area of study

In September-October 1997 four sites on the Suir Estuary were sampled. Each site contained midlittoral sediments and a contiguous salt marsh area (Table 1, Figure 1). In October-November 1998 the study area was extended and eight sites containing midlittoral sediments were sampled (Table 1, Figure 2).

**Table 1.** Location of sites on the Suir Estuary in 1997 and 1998.

| site | coordinates 1997 | coordinates 1998 | distance from Killoteran[1] (km) |
|---|---|---|---|
| Killoteran | | S 544 106 | 0 |
| Granagh | S 587 142 | S 587 142 | 4.6 |
| Johns River | | S 614 124 | 7.1 |
| Maypark | S 635 118 | S 635 118 | 8.9 |
| Belview | S 654 122 | S 654 122 | 10.2 |
| Ballinakill | | S 647 103 | 10.2 |
| Cheekpoint | S 683 137 | S 683 137 | 12.5 |
| Passage East | | S 701 103 | 15.8 |

Source: Ordnance Survey of Ireland: 1/50,000 Discovery Series, number 76.
[1]Killoteran is located at the freshwater-saltwater interface on the Suir Estuary.

## Analysis of sediments

See Chapter 3 for details of sampling and analysis of midlittoral sediments and salt marsh sediments for Cu, Pb and Cr concentrations and also for particle size < 63 µm and organic matter content.

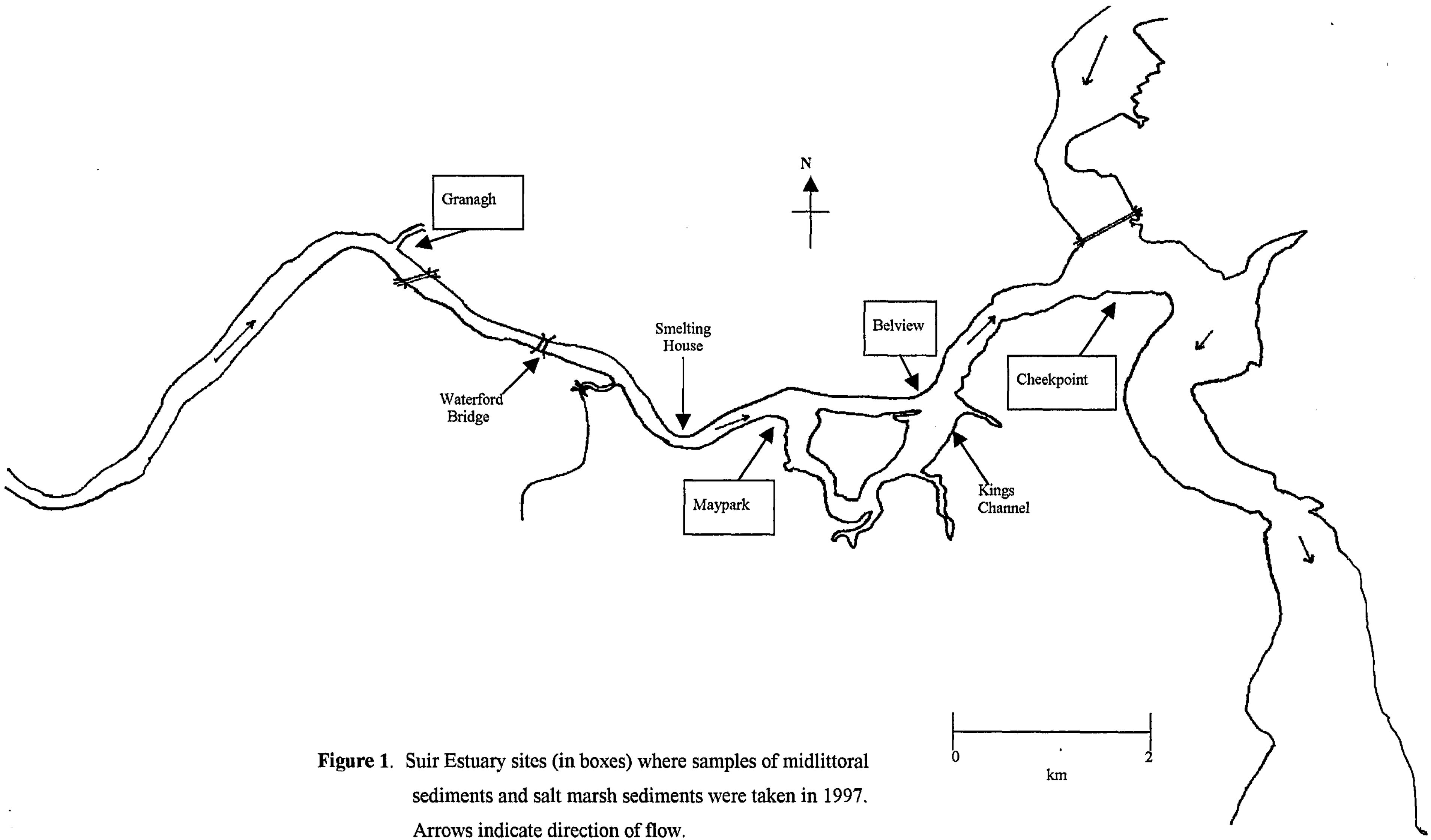



**Figure 1**. Suir Estuary sites (in boxes) where samples of midlittoral sediments and salt marsh sediments were taken in 1997. Arrows indicate direction of flow.

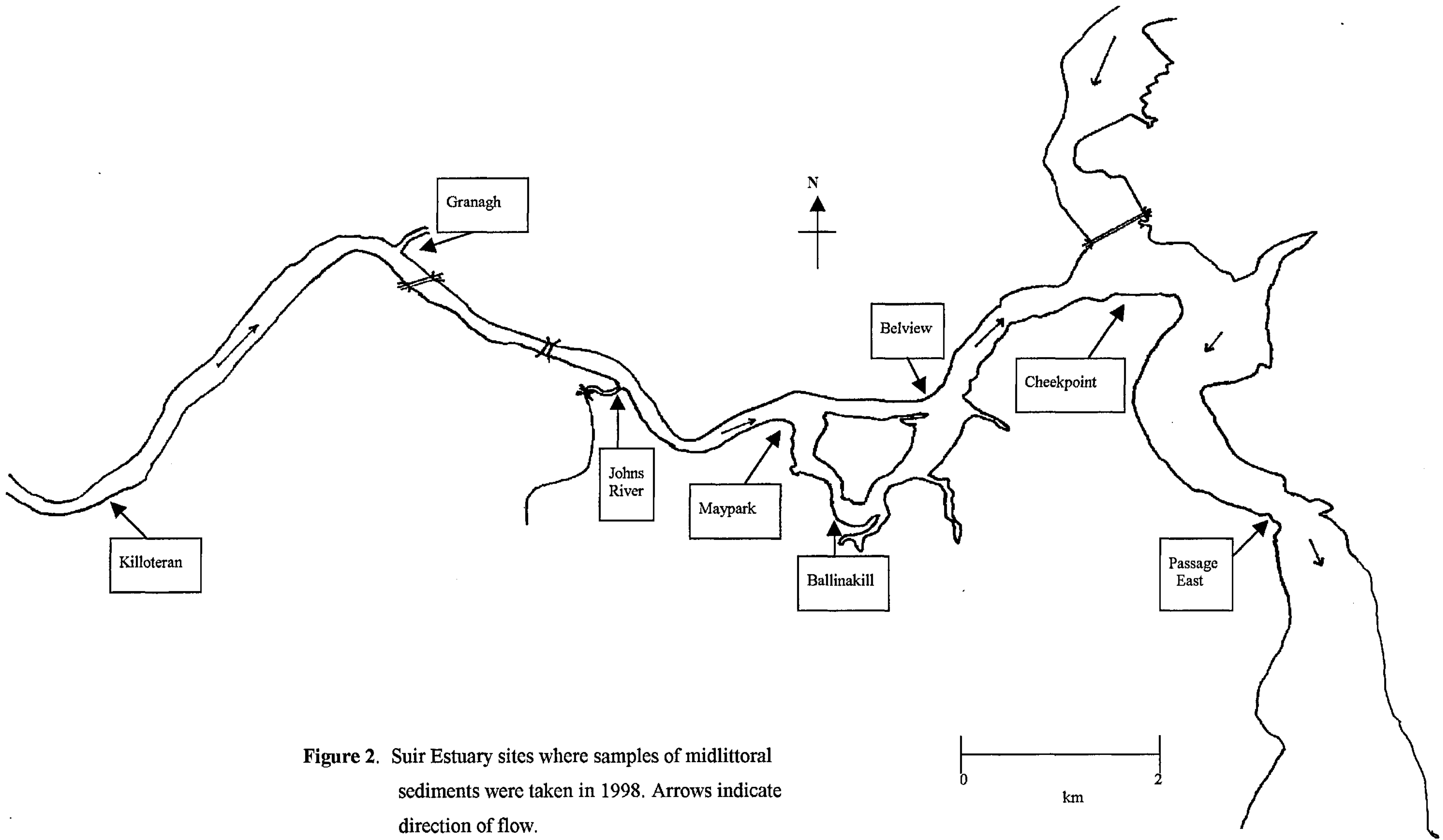



**Figure 2.** Suir Estuary sites where samples of midlittoral sediments were taken in 1998. Arrows indicate direction of flow.

# RESULTS

## Upper and lower Suir Estuary

Mean concentrations of Cu, Pb and Cr in midlittoral sediments were recorded at eight sites along the Suir Estuary in 1998 (Table 2). From this data it was possible to compare concentrations of each metal throughout the Suir Estuary (i.e. from the freshwater-saltwater interface at Killoteran to Passage East in the lower estuary). Cu concentrations (range 7.6 – 15.0 mg $kg^{-1}$) were low compared

**Table 2.** Mean metal concentrations (mg $kg^{-1}$), f < 63 µm, and loss on ignition of midlittoral sediments at eight sites on the Suir Estuary in 1998. Standard deviations are shown in brackets. Values with different letters within a column per metal per seaweed species are significantly different (Tukey test). The number of replications is four.

| | **Cu** (mg $kg^{-1}$) | **Pb** (mg $kg^{-1}$) | **Cr** (mg $kg^{-1}$) | **f < 63 µm** (%) | **LOI** (%) |
|---|---|---|---|---|---|
| Killoteran | 14.1 (2.2) *ab* | 43.7 (12.3) *ac* | 34.4 (12.8) *ab* | 67 (11.5) *ab* | 17 (1.9) *a* |
| Granagh | 14.3 (0.7) *ab* | 52.9 (3.1) *ab* | 42.8 (3.3) *a* | 63 (8.4) *ab* | 14 (1.1) *ab* |
| Johns River | 15.0 (0.9) *a* | 63.4 (4.5) *b* | 42.3 (10.3) *a* | 52 (9.3) *a* | 15 (2.1) *a* |
| Maypark | 11.0 (1.8) *bc* | 40.7 (6.0) *ac* | 27.6 (4.6) *ac* | 74 (7.3) *ab* | 12 (1.3) *ab* |
| Belview | 9.6 (1.8) *c* | 34.7 (3.7) *c* | 23.1 (3.9) *bc* | 64 (6.4) *ab* | 16 (1.1) *a* |
| Ballinakill | 12.5 (0.9) *ac* | 36.3 (2.5) *c* | 24.4 (5.0) *bc* | 77 (1.6) *b* | 14 (1.8) *a* |
| Cheekpoint | 9.5 (0.6) *ce* | 21.2 (1.7) *d* | 14.1 (4.7) *c* | 55 (5.3) *ac* | 14 (0.8) *a* |
| Passage East | 7.6 (1.9) *de* | 14.7 (3.7) *d* | 14.7 (3.2) *c* | 40 (19.0) *c* | 9 (4.1) *b* |

Limits of detection: Cu 0.7 mg $kg^{-1}$, Pb 1.1 mg $kg^{-1}$, Cr 0.7 mg $kg^{-1}$, dry weight.

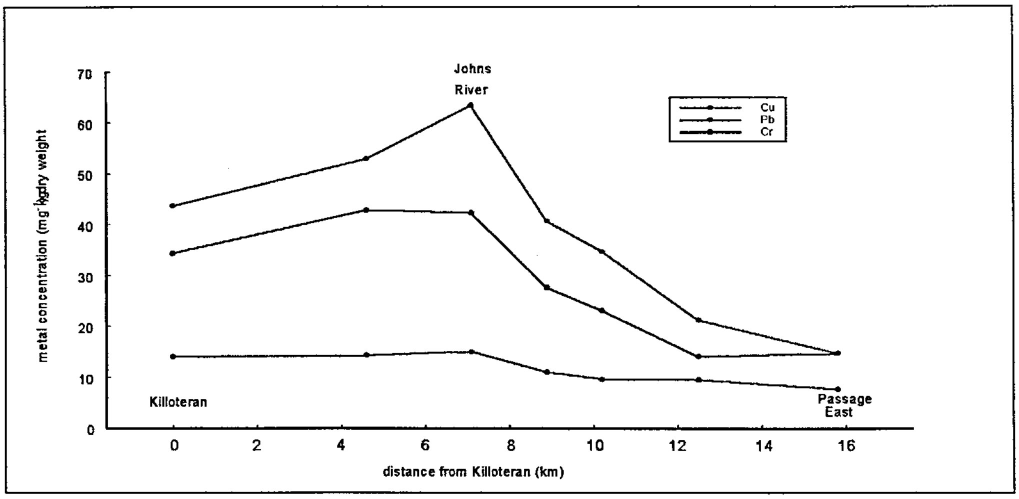



**Figure 3**. Metal concentrations (mg $kg^{-1}$ dry weight) in midlittoral sediments along the Suir Estuary 1998.

to the other metals and showed a slight decrease with progress toward the lower estuary (Table 2, Figure 3). Pb concentrations (range 14.7 – 63.4 mg $kg^{-1}$) were the highest of the three metals throughout the Suir Estuary. The concentrations decreased downstream after a significant rise at Johns River. Cr concentrations (range 14.1 – 42.8 mg $kg^{-1}$) also decreased toward the lower estuary after the highest concentrations were recorded at Granagh and Johns River. There were very significant correlations ($P < 0.01$) between all three metal concentrations in the Suir Estuary (Table 3). Cu was the only metal that correlated ($P < 0.05$) with the organic matter content (LOI). The sediment particle size f < 63 μm correlated with LOI ($P < 0.05$) but not with any of the metals. There was no correlation between f < 63 μm and distance downstream on the estuary from the FSI at Killoteran (Figure 4). There was very large intra- as well as inter-site variation in particle size fraction < 63 μm.

**Table 3.** Pearson product-moment correlation coefficients (r) for correlations between metal concentrations, f< 63 μm, and loss on ignition in midlittoral sediments at sites on the Suir Estuary in 1998. n = 8 sites (4 replications per site).

| | Pb | Cr | f< 63 μm | LOI |
|---|---|---|---|---|
| Cu | + 0.87** | + 0.84** | + 0.33 | + 0.53* |
| Pb | | + 0.93** | + 0.26 | + 0.44 |
| Cr | | | + 0.18 | + 0.39 |
| f< 63 μm | | | | + 0.58* |

**P < 0.01 *P < 0.05

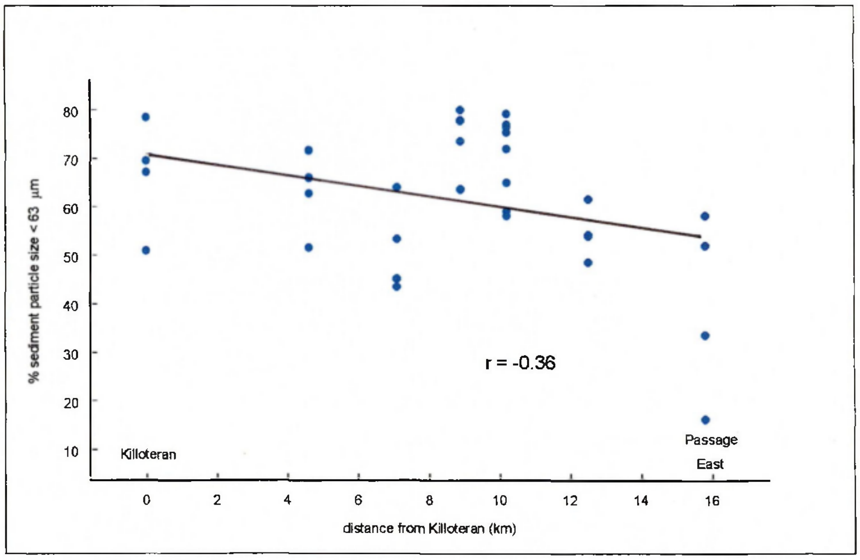



**Figure 4.** Relationship between midlittoral sediment particle size < 63 μm and distance downstream from Killoteran on the Suir Estuary in 1998.

r = product-moment correlation coefficient P < 0.05

## Comparisons of midlittoral sediments 1997 and 1998

Comparisons of metal concentrations between 1997 and 1998 were made at four sites (Table 4). A decrease in metal concentrations from the upper to the lower estuary was recorded in both years. The metal concentration trends downstream in the Suir Estuary were surprisingly similar, except for Cr at Belview, between 1997 and 1998 and there was a high degree of correlation for all three metals between the two years (Figure 5). Two-way analysis of variance indicated that there were significant differences ($P < 0.001$) between sites for all three metals (Table 5). There were also significant differences between sites for the sediment fraction < 63 um ($P < 0.01$) and to a lesser extent for organic matter content ($P < 0.05$). There were no significant differences between 1997 and 1998 for any of the metals, for f < 63 μm, or for organic matter content.

**Table 4.** Comparison of mean metal concentrations (mg $kg^{-1}$) of midlittoral sediments in 1997 and 1998. Standard deviations are shown in brackets. Values with different letters within a column per metal per seaweed species are significantly different (Tukey test). The number of replications is four.

**1997**

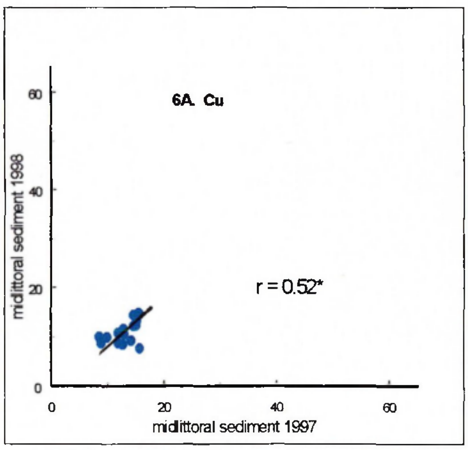
| | Cu (mg $kg^{-1}$) | Pb (mg $kg^{-1}$) | Cr (mg $kg^{-1}$) |
|---|---|---|---|
| Granagh | 15.3 (0.5) *a* | 52.2 (3.5) *a* | 39.1 (2.4) *a* |
| Maypark | 13.6 (1.5) *ab* | 42.6 (3.3) *b* | 33.1 (7.4) *ab* |
| Belview | 13.4 (1.6) *ab* | 39.7 (2.1) *b* | 41.7 (13.9) *a* |
| Cheekpoint | 10.4 (2.6) *b* | 27.3 (5.9) *c* | 18.0 (3.8) *b* |

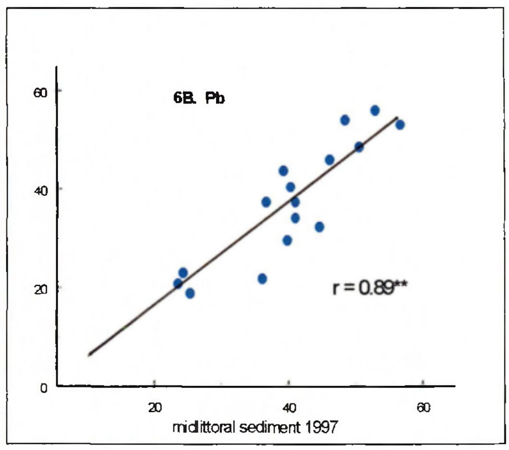
**Table 4 continued:**

**1998**

| | **Cu** (mg kg$^{-1}$) | **Pb** (mg kg$^{-1}$) | **Cr** (mg kg$^{-1}$) |
|---|---|---|---|
| Granagh | 14.3 (0.7) *a* | 52.9 (3.1) *a* | 42.8 (3.3) *a* |
| Maypark | 11.0 (1.8) *b* | 40.7 (6.0) *b* | 27.6 (4.6) *b* |
| Belview | 9.6 (1.8) *b* | 34.7 (3.7) *b* | 23.1 (3.9) *b* |
| Cheekpoint | 9.5 (0.6) *b* | 21.2 (1.7) *c* | 14.1 (4.7) *c* |

Limits of detection: Cu 0.7 mg kg$^{-1}$, Pb 1.1 mg kg$^{-1}$, Cr 0.7 mg kg$^{-1}$, dry weight.



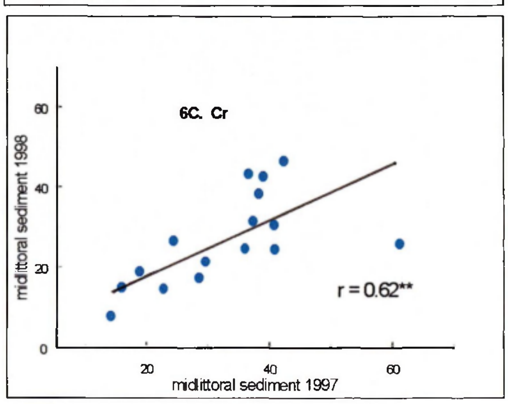




Figure 5. Relationships between metal concentrations in midlittoral sediments in 1997 and 1998 on the Suir Estuary.
Straight lines represent regression lines

r = product-moment correlation coefficient
**P < 0.01 *P < 0.05

**Table 5.** Results of two-way analysis of variance for differences in Cu, Pb and Cr concentrations in midlittoral sediments between sites and between 1997 and 1998.

| | Between years | Between sites | Interaction |
|---|---|---|---|
| Cu | * | *** | *** |
| Pb | n.s. | *** | *** |
| Cr | n.s. | *** | *** |
| f < 63 µm | n.s. | ** | ** |
| LOI | n.s. | * | n.s. |

n.s. = not significant ***P < 0.001 **P < 0.01 *P < 0.05

**Comparison of intertidal sediments and salt marsh sediments**

A comparison of metal concentrations, f < 63 µm and organic matter content between midlittoral sediment and salt marsh sediment taken from between the roots of *A. tripolium* was made at four sites in 1997 (Table 6, Figure 6). There were no significant differences between metal concentrations in midlittoral and salt marsh sediments. Cu concentrations (range 10.4 – 15.3 mg $kg^{-1}$) and Pb concentrations (range 27.3 – 52.2 mg $kg^{-1}$) in salt marsh sediments correlated to a high degree ($P < 0.01$) with concentrations of these metals in midlittoral sediments (Figure 7). There was a lesser correlation ($P < 0.05$) between Cr concentrations in the two sediments types. Two-way analysis of variance indicated no differences between midlittoral sediment and salt marsh sediment for any of the metals, f < 63 µm and organic matter content (Table 7). There were significant differences between sites for all factors.

**Table 6.** Mean metal concentrations (mg $kg^{-1}$), f < 63 µm, and the loss on ignition of midlittoral sediments and salt marsh sediment samples in 1997. Standard deviations are shown in brackets. Values with different letters within a column are significantly different (Tukey test). The number of replications is four.

**Midlittoral sediments**

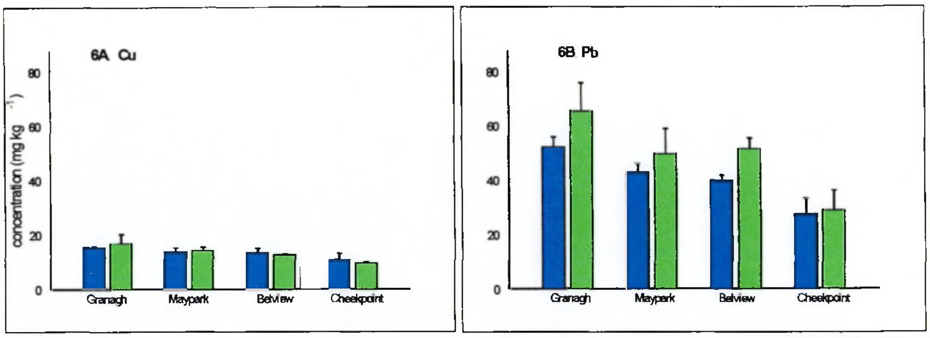
| | **Cu** (mg $kg^{-1}$) | **Pb** (mg $kg^{-1}$) | **Cr** (mg $kg^{-1}$) | **f < 63 µm** (%) | **LOI** (%) |
|---|---|---|---|---|---|
| Granagh | 15.3 (0.5) *a* | 52.2 (3.5) *a* | 39.1 (2.4) a | 75 (8.7) *a* | 19 (0.3) *a* |
| Maypark | 13.6 (1.5) *ab* | 42.6 (3.3) *b* | 33.1 (7.4) *ab* | 65 (12.5) *a* | 15 (1.1) *ab* |
| Belview | 13.4 (1.6) *ab* | 39.7 (2.1) *b* | 41.7 (3.9) a | 37 (15.4) *b* | 14 (3.8) *ab* |
| Cheekpoint | 10.4 (2.6) *b* | 27.3 (5.9) *c* | 18.0 (3.8) b | 55 (10.1) *ab* | 10 (2.7) *b* |

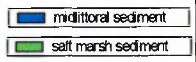
**Salt marsh sediments**

| | **Cu** (mg $kg^{-1}$) | **Pb** (mg $kg^{-1}$) | **Cr** (mg $kg^{-1}$) | **f < 63 µm** (%) | **LOI** (%) |
|---|---|---|---|---|---|
| Granagh | 16.6 (3.6) *a* | 65.3 (10.6) *a* | 56.0 (20.1) *a* | 77 (3) *a* | 20 (1) *a* |
| Maypark | 14.2 (1.3) *ab* | 49.5 (9.5) *a* | 35.4 (7.3) *a* | 70 (7) *a* | 21 (4) *a* |
| Belview | 12.4 (0.7) *bc* | 51.5** (3.8) *a* | 47.9 (16.9) *a* | 38 (11) *b* | 17 (4) *ab* |
| Cheekpoint | 9.4 (0.6) *c* | 28.8 (7.3) *b* | 26.7 (8.1) *a* | 49 (8) *c* | 11 (2) *bc* |

** metal concentration in salt marsh sediment was significantly higher than metal concentration in midlittoral sediment (two tailed t-test, P = 0.01).

Limits of detection: Cu 0.7 mg $kg^{-1}$, Pb 1.1 mg $kg^{-1}$, Cr 0.7 mg $kg^{-1}$, dry weight.



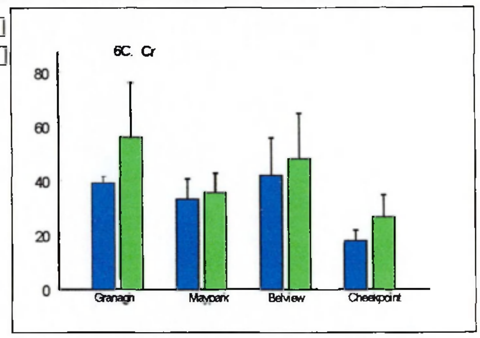
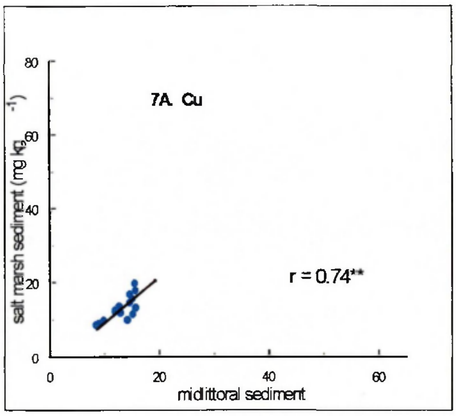




**Figure 6.** Comparison of mean values of Cu and Pb concentrations ($mg\ kg^{-1}$ dry weight) in midlittoral sediments and sediment from between the roots of *Aster tripolium* at sites on the Suir Estuary in 1997. n = 4 replications

**Table 7.** Results of two-way analysis of variance for differences in metal concentrations, f < 63 µm, and loss on ignition, between sites, and between midlittoral sediments and salt marsh sediments, in 1997.

| | Between midlittoral & salt marsh sediments | Between sites | Interaction |
|---|---|---|---|
| Cu | n.s. | *** | *** |
| Pb | n.s. | *** | *** |
| Cr | n.s. | *** | *** |
| f < 63 µm | n.s. | *** | *** |
| LOI | n.s. | *** | *** |

n.s. = not significant ***P < 0.001



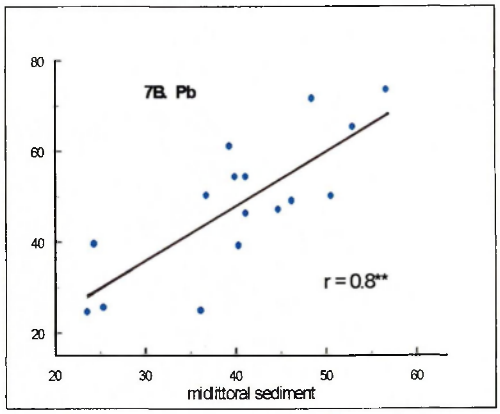
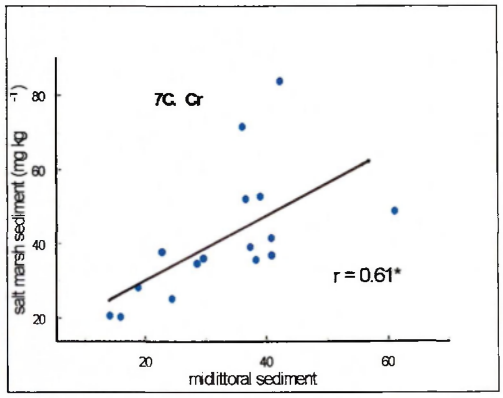




Figure 7. Relationships between metal concentrations in midittoral sediments and salt marsh sediments on the Suir Estuary in 1997.
Straight lines represent regression lines.

r = product-moment correlation coefficients
**p < 0.01 *p < 0.05




There was a highly significant correlation between midlittoral sediments and salt marsh sediments for each of the metals (Table 8). There was no correlation between metal concentrations and particle size < 63 µm, except in the case of Cu in salt marsh soil ($P < 0.05$). There was significant correlation between organic matter content and all three metals and with particle size < 63 µm in midlittoral sediments only.

**Table 8.** Pearson product-moment correlation coefficients (r) for correlations between Cu and Pb concentrations, fraction of sediment less than 63 µm, and loss on ignition in midlittoral sediments and salt marsh sediments taken from between the roots of *Aster tripolium* in 1997. n = 4 sites (4 replications per site).

**Midlittoral sediments**

| | Pb | Cr | f < 63 µm | LOI |
|---|---|---|---|---|
| Cu | + 0.86** | + 0.81** | + 0.42 | + 0.58* |
| Pb | | + 0.63** | + 0.42 | + 0.68** |
| Cr | | | + 0.13 | + 0.52* |
| f < 63 µm | | | | + 0.64** |

**Salt marsh sediments**

| | Pb | Cr | f < 63 µm | LOI |
|---|---|---|---|---|
| Cu | + 0.89** | + 0.66** | + 0.61* | + 0.63** |
| Pb | | + 0.63** | + 0.38 | + 0.70** |
| Cr | | | + 0.18 | + 0.29 |
| f < 63 µm | | | | + 0.47 |

**P < 0.01 *P < 0.05

**Table 9.** Mean concentrations of metals (mg $kg^{-1}$) in midlittoral sediments along the Suir Estuary in 1997.

| | **Cu (mg $kg^{-1}$)** | **Pb (mg $kg^{-1}$)** | **Cr (mg $kg^{-1}$)** |
|---|---|---|---|
| Waterford Bridge | 17.9 | 31.7 | 43.4 |
| Smelting House | 13.7 | 30.4 | 42.3 |
| Kings Channel | 17.4 | 23.2 | 30.7 |
| Cheekpoint | 13.6 | 28.2 | 38.0 |

Source: Neill, 1998.

# DISCUSSION

The high correlation between the three metals suggests similar deposition patterns and is in agreement with findings by Zwolsman *et al.* (1996) in the Scheldt Estuary. There was a significant decrease in concentrations of Cu, Pb and Cr in midlittoral sediments, from the upper to the lower Suir Estuary, in 1998. This is in agreement with research findings in estuaries elsewhere (Attrill & Thomes, 1995; Zwolsman *et al.*, 1996; Wright & Mason, 1999). There can be a number of reasons for elevated metal concentrations in the upper estuary. The dilution of contaminated sediments with relatively clean marine sediments further downstream can be an important factor. The release of metals to the water column in the freshwater-saltwater interface (FSI) is also an important factor. Other research in this study (Chapter 7) has demonstrated that the concentration of Cu in water increases with increasing salinity, (i.e. downstream). This is because the binding of Cu to sediment is decreased due to competition from $Ca^{2+}$ and $Mg^{2+}$ (Mantoura *et al.*, 1978; Liu *et al.*, 1998).

The highest Pb concentrations were recorded at the mouth of Johns River which is located approximately eight kilometres downstream of the freshwater-saltwater interface. The Pb peak recorded at Johns River may be an indication of serious contamination from sources upstream in that tributary and this is confirmed by Pb concentrations recorded in seaweed samples collected from the site (Chapter 7). Further investigation of metal concentrations (Pb in particular), upstream in Johns River, is required to locate the source, or sources, of pollution.

The higher Cr concentrations in the upper estuary are most likely to have resulted from anthropogenic pollution from both old and new sources. Derelict tanneries situated upriver, closed in 1985, had poor control systems to contain the large quantities of chromium oxide used. This Cr would have been adsorbed onto basal sediments but can be remobilised in the Suir Estuary by physical disturbances from tidal action, storms, boat traffic, dredging and bioturbation (Bubb & Lester, 1991; Fletcher *et al.*, 1994).

There was close agreement between metal concentrations in midlittoral sediments recorded in 1997 and 1998. The 1997 metal concentrations in midlittoral sediments recorded in this study were in general agreement with Neill (1998), who also analysed midlittoral sediment samples from a number of sites on the Suir Estuary in 1997.

There were no significant differences in 1997 between midlittoral sediments and salt marsh sediment taken from between the roots of *A. tripolium*, for all of the characteristics measured (i.e. metal concentrations, f < 63 um and organic matter content), except in the case of Pb concentrations which were higher in salt marsh sediments at the Belview site. The close agreement between metal concentrations in midlittoral and salt marsh sediments (with the exception of Pb concentrations at Belview), appears to conflict with previous research by Fletcher *et al.* (1994) and Wright & Mason (1999) who found that the presence of salt marsh vegetation resulted in higher organic material being added to the sediment and this increased metal retention. However, the organic matter contents of the midlittoral sediments and salt marsh sediments in this study were very similar. Perhaps the pattern of organic matter accumulation for both sediments was similar as they were situated relatively close to each other (approximately 2-10 metres apart at different sites), but this needs further investigation.

There was a high degree of correlation between organic matter content and metal concentrations in both midlittoral and salt marsh sediments and this confirms previous research (Beeftink *et al.*, 1982; Otte *et al.*, 1991, 1993; Harland *et al.*, 2000). The only exception was Cr in salt marsh sediment, which displayed high intra-site variation. Research by Wright & Mason (1999) has shown that maximum concentrations of metals in salt marsh sediments are found in winter. This is due to the loss of metals from the root system due to excretion or degradation of underground biomass (Caçador *et al.*, 2000). Sampling of sediments for this study was carried out during September-October 1997 and

October-November 1998 when salt marsh plants were already showing signs of advanced decay.

The increased organic matter content of the salt marsh sediments resulting from the degradation of plant tissue increases the cation exchange capacity of the sediment and the tendency of transition metal cations to form stable complexes with organic ligands (Elliott *et al.*, 1986). These researchers also reported that Cu forms the most stable organic complexes among the transition metals and that Pb retention may be relatively unaffected by organic matter. Reboredo (1993) found that much of the Cu in soils is in forms unavailable to plants as it forms strong complexes with fulvic and humic acids. The close correlation between organic matter content and Cu concentrations was confirmed by this study in both years and for both midlittoral and salt marsh sediments. Pb concentrations correlated with organic matter content in both sediment types in 1997, but not in 1998, indicating a less stable binding of Pb. Cr is more readily retained by the sediment during shifts from oxidising to reducing conditions, due to tidal inundations, than most other metals (Zwolsman *et al.*, 1993). Cr adsorption seems to be less influenced by the organic matter content of sediment than Cu or Pb. Bryan & Langston (1992) reported that Cr appears to be largely associated with oxides of Fe in sediment.

There was no correlation between any of the metal concentrations and particle size < 63 μm in the midlittoral sediments. Otte (1991) reported that, in general, the mobility of metals decreases with an increasing fraction of particles < 63 μm due to adsorption of the metals to these smaller particles. However, Otte *et al.*

(1991) also found no correlation between metal concentrations and particle size < 63 μm in a number of salt marshes in Holland. In this study the proportion of sediment particles < 63 μm remained high and fairly similar throughout most of the Suir Estuary with the exception of the two sites furthest downstream (Cheekpoint and Passage East) when the larger sandy grains start to predominate. This non-linear reduction in particle size < 63 μm could account for the poor correlation between metal concentrations and f < 63 μm.

# CHAPTER 6

# Copper and lead concentrations in salt marsh plants on the Suir Estuary, Ireland*

*E.J. Fitzgerald, J.M. Caffrey, S.T. Nesaratnam & P. McLoughlin

# SUMMARY

Concentrations of Cu and Pb were determined in the roots and shoots of six salt marsh plant species, and in sediment taken from between the roots of the plants, sampled from the lower salt marsh zone at four sites along the Suir Estuary in autumn 1997. Cu was mainly accumulated in the roots of monocotyledonous and dicotyledonous species. Pb was mainly accumulated in the roots of monocotyledons, while dicotyledons tended to accumulate Pb in the shoots. In the case of *Aster tripolium* there was a clear differentiation in the partitioning of Pb within the plant, between low and high salinity sites. At the low salinity sites, Pb accumulated only in the roots while at the high salinity sites there was a marked translocation to the shoots. The increase in Pb concentrations in roots and shoots of *A. tripolium* was accompanied by a concomitant decrease in sediment concentrations of Pb. This inverse correlation between sediment and plant concentrations of Pb was also recorded for *Spartina* spp. and *Schoenoplectus tabernaemontani* but in the case of these species the roots contained the higher concentrations of Pb regardless of salinity levels. These differences in accumulation of Cu and Pb in various salt marsh species, and the influence of salinity on the translocation of Pb in *A. tripolium* in particular, should be taken into account when using these plants for biomonitoring purposes.

## INTRODUCTION

Salt marshes act as sinks for anthropogenically derived metal contaminants. Metal concentrations in salt marsh sediments depend on complex physico-chemical and biogeochemical reactions which are influenced by metal speciation, salinity, pH, redox potential of the sediment, organic matter content of the sediment, particle size, and the presence of vegetation (Fletcher *et al.*, 1994; Williams *et al.*, 1994a; Otte *et al.*, 1993; Doyle & Otte, 1997; Caçador *et al.*, 2000).

The dominant uptake pathway for most salt marsh plants from the sediment is via the root system with subsequent acropetal translocation from the root to the aerial parts (Rozema *et al.*, 1988). Consequently most metals tend to accumulate in the roots rather than in shoots. However, there is a high degree of variability between metals and between various plant species (Reboredo, 1993; Williams *et al.*, 1994b). Otte *et al.* (1991) found that dicotyledonous species tended to have similar metal concentrations in roots and shoots, whereas in monocotyledonous species the concentrations in roots were higher than in shoots. Several other factors also affect the uptake of heavy metals, including differences in age and growth stages, seasonal variations, presence of iron plaques on the roots, level of metal contamination in the locality, soil properties, tidal inundations and salinity (Gleason *et al.*, 1979; Beeftink *et al.*, 1982; Rozema *et al.*, 1990; Otte *et al.*, 1989, 1991, 1993; Williams *et al.*,1994a; Sundby *et al.*, 1998; Caçador *et al.*, 2000). Salinity has also been shown to be a key factor in the translocation of metals from roots to shoots in *Aster tripolium* (Otte, 1991).

The main purpose of the study was to compare the concentrations of Cu and Pb in roots and shoots of a number of plant species taken from salt marshes along the Suir estuary. A number of factors that influence the use of salt marsh plant species for biomonitoring purposes are discussed. Sediment samples taken from between the roots of the plants were also analysed for Cu and Pb concentrations and interactions between sediment and plant metal concentrations are discussed. Pb was chosen for investigation because of previous reports of elevated concentrations in intertidal sediments at sites on the Suir Estuary (Neill, 1998). Cu was chosen as a general indicator of industrial and domestic pollution.

## MATERIALS AND METHODS

**Area of study**

Four salt marsh sites along the inner Suir Estuary were identified for study (Figure 1). The sites are located at the following map coordinates*:

| | |
|---|---|
| Granagh | S 587 142 |
| Maypark | S 635 118 |
| Belview | S 654 122 |
| Cheekpoint | S 683 137 |

*Ordnance Survey of Ireland: 1/50,000 Discovery series, number 76

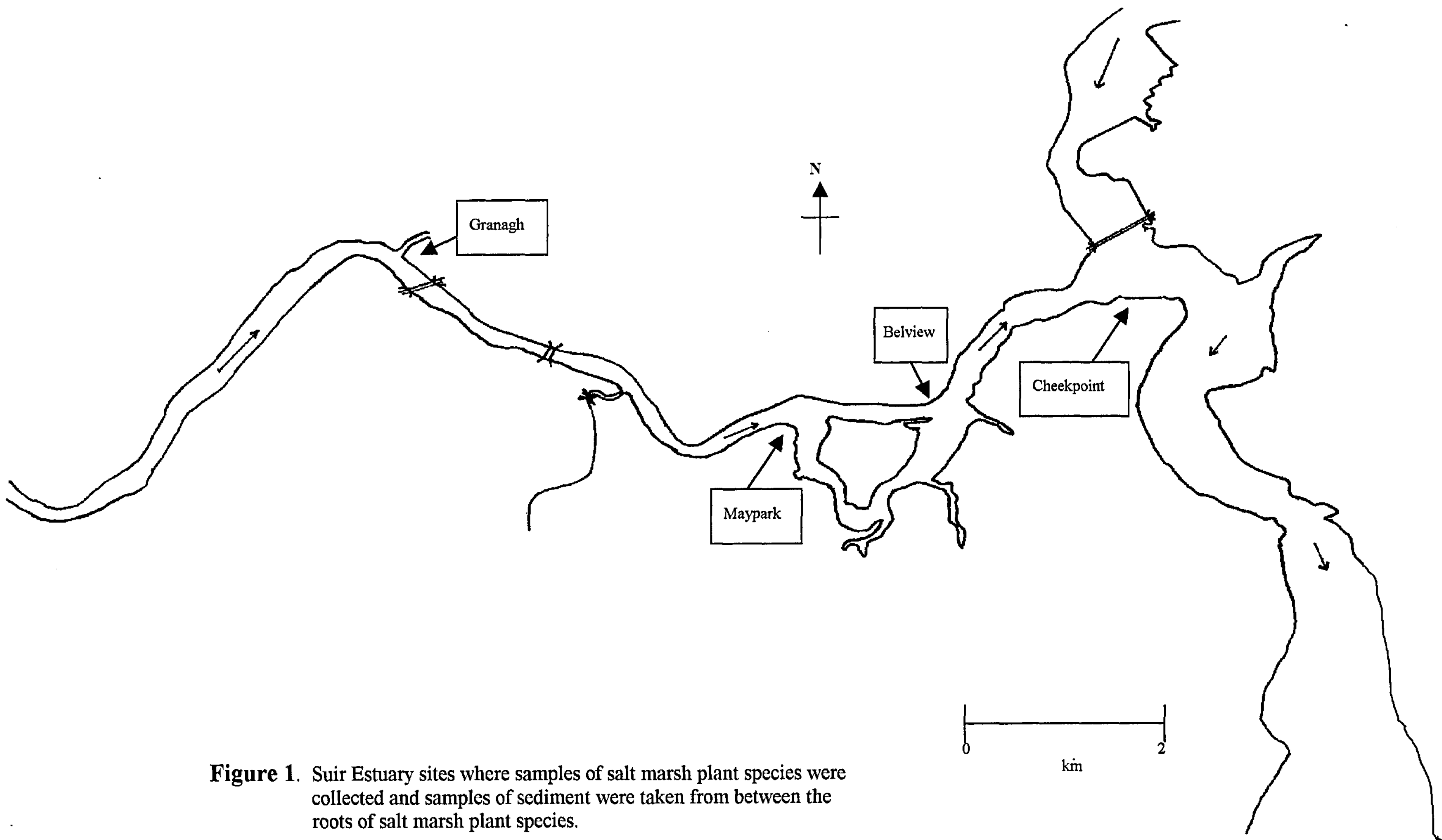



**Figure 1**. Suir Estuary sites where samples of salt marsh plant species were collected and samples of sediment were taken from between the roots of salt marsh plant species.

**Plant samples**

Plant specimens were lodged with the Herbarium, National Botanic Gardens, Dublin, and identification confirmed. The *Spartina* genus is well known for its genetic elasticity. On the Suir Estuary the sterile form, *S. x townsendii*, was found at the Belview and Cheekpoint sites while the fertile form, *S. anglica*, was found at Maypark. Amphidiploid and polyhaploid forms of *Spartina* were also found at a nearby site on the Suir Estuary, not included in this study (M. Jebb, personal communication). Because of the possibility that a number of *Spartina* species co-existed on the same sites, they are referred to collectively as *Spartina* spp. in this study.

**Analysis of plant material**

Sampling of plants was carried out at the four salt marsh sites in September-October 1997. Four plants of each species were collected at each salt marsh and the roots and shoots separated. They were then transported to the laboratory in plastic bags and frozen at $-10^{0}$C until analysis. See Chapter 3 for details of analysis of plant material for Cu and Pb concentrations.

**Analysis of sediment**

A sample of sediment was taken from between the roots of each plant, at the same time as the plants were sampled, at the four salt marshes. See Chapter 3 for details of analysis of sediment for Cu and Pb concentrations and also for particle size < 63 μm and organic matter content.

### Analysis of sediment porewater

Salinity measurements of four sediment porewater samples taken from each site were recorded using the method outlined in Chapter 3.

## RESULTS

### Sediment characteristics and metal concentrations

The organic matter content (LOI) decreased downstream in sediment taken from between the roots of *A. tripolium* and *Spartina* spp. (Table 1). The only significant differences in particle size < 63 μm between sites was recorded in

**Table 1.** Mean and standard deviation of Cu and Pb concentrations in sediment samples collected from between the roots of plant species, the fraction of soil particles smaller than 63 μm, and the loss on ignition of the sediment samples, at salt marsh sites along the Suir Estuary in Sept-Oct 1997. Standard deviations are shown in brackets. Values with different letters within a column per metal per plant species are significantly different (Tukey test). The number of replications is four.

| site | Cu ($\mu$mol kg$^{-1}$) | Pb ($\mu$mol kg$^{-1}$) | f < 63μm (%) | LO1 (%) |
|---|---|---|---|---|
| **Dicotyledons** | | | | |
| *Aster tripolium* (sediment) | | | | |
| Granagh | 261.4 (56.7) *a* | 315.2 (51.2) *a* | 77 (3) *a* | 20 (1) *a* |
| Maypark | 223.6 (20.5) *ab* | 238.9 (45.9) *a* | 70 (7) *a* | 21 (4) *a* |
| Belview | 195.3 (11.0) *bc* | 248.6 (18.3) *a* | 38 (11) *b* | 17 (4) *ab* |
| Cheekpoint | 148.0 (9.5) *c* | 139.0 (35.2) *b* | 49 (8) *c* | 11 (2) *bc* |

**Table 1 continued:**

| | | | | |
|---|---|---|---|---|
| *Plantago maritima* (sediment) | | | | |
| Maypark | 195.3 (157.5) *a* | 187.7 (29.9) *a* | 48 (17) *a* | 21 (6) *a* |
| Belview | 252.0 (99.2) *a* | 211.4 (51.2) *a* | 36 (11) *a* | 17 (1) *a* |
| Cheekpoint | 137.0 (15.8) *a* | 150.6 (15.4) *a* | 50 (7) *a* | 13 (1) *a* |
| **Monocotyledons** | | | | |
| *Phragmites australis* (sediment) | | | | |
| Granagh | 252.0 (77.2) | 277.0 (67.1) | 69 (8) | 19 (3) |
| *Schoenoplectus tabernaemontani* (sediment) | | | | |
| Granagh | 365.4 (41.0) *a* | 334.0 (30.4) *a* | 72 (7) *a* | 17 (2) *a* |
| Maypark | 242.5 (23.6) *b* | 270.3 (42.0) *b* | 60 (12) *a* | 21 (3) *a* |
| *Spartina spp.* (sediment) | | | | |
| Maypark | 168.5 (31.5) *ab* | 195.0 (62.7) *a* | 62 (10) *a* | 19 (4) *a* |
| Belview | 196.9 (17.3) *a* | 215.3 (24.1) *a* | 60 (8) *a* | 12 (2) *b* |
| Cheekpoint | 133.9 (15.8) *b* | 134.7 (7.2) *a* | 52 (8) *a* | 12 (2) *b* |
| *Agrostis stolonifera* (sediment) | | | | |
| Maypark | 195.3 (17.3) *a* | 209.0 (47.3) *a* | 63 (8) *a* | 14 (4) *a* |
| Cheekpoint | 129.1 (7.9) *b* | 131.3 (19.8) *b* | 55 (2) *a* | 11 (1) *a* |

Limits of detection: Cu 4.7 $\mu$mol kg$^{-1}$, Pb 66.1 $\mu$mol kg$^{-1}$, dry weight.

sediment from between the roots of *A. tripolium*. There was an overall decrease in sediment concentrations of Cu and Pb from Granagh (low salinity), to Cheekpoint (high salinity).

There was a very high correlation ($P < 0.01$) between Cu and Pb concentrations in the salt marsh sediments taken from between the roots of all plant species (Table 2). Organic matter content of the sediments and particle size < 63 μm also correlated significantly with concentrations of both metals.

**Table 2.** Pearson product-moment correlation coefficients (r) for Cu and Pb concentrations, f < 63 μm, and LOI of sediment samples collected from between the roots of all plant species sampled. n = 4 sites (4 replications per site).

| | Cu | Pb |
|---|---|---|
| Pb | + 0.82** | |
| LOI | + 0.39** | + 0.53** |
| f < 63 μm | + 0.32* | + 0.40** |

**P < 0.01 *P < 0.05

**Metal concentrations in plants**

Monocotyledonous species, with the exception of *P. australis*, contained higher concentrations of Pb in the roots compared to shoots, though differences were not significant for all sites (Table 3). Shoot-to-root ratios for Cu and Pb concentrations were calculated for each of the species at each site (Table 4). In the case of dicotyledonous species, in particular *A. tripolium*, there was a notable increase in shoot-to-root ratios for both Cu and Pb as salinity increased along the Suir Estuary. The trend was less marked in the case of the monocotyledonous species.

**Table 3.** Mean Cu and Pb concentrations (µmol kg$^{-1}$ dry weight) in shoots and roots of plant species from saltmarsh sites on the Suir Estuary. Significant differences between shoot and root concentrations were tested using the t-test. Standard deviations are shown in brackets. Values with different letters within a column per metal per plant species are significantly different (Tukey test). The number of replications is four for each plant species.

| | **Cu** | | **Pb** | |
|---|---|---|---|---|
| **site** | **shoot (µmol kg$^{-1}$)** | **root (µmol kg$^{-1}$)** | **shoot (µmol kg$^{-1}$)** | **root (µmol kg$^{-1}$)** |
| **Dicotyledons** | | | | |
| *Aster tripolium* | | | | |
| Granagh | 7.9 (11.0) *a* | 50.4** (17.3) *a* | < | 84.0** (63.2) *a* |
| Maypark | 47.2 (1.0) *b* | 78.7** (37.8) *a* | < | 114.9** (61.3) *a* |
| Belview | 92.9 (25.2) *c* | 119.7 (3.4) *a* | 112.5 (20.8) *a* | 98.0 (18.3) *a* |
| Cheekpoint | 80.3 (1.6) *bc* | 50.4 (26.8) *a* | 360.5** (76.3) *b* | 239.9 (41.0) *b* |
| *Plantago maritima* | | | | |
| Maypark | 28.4 (22.1) *a* | 67.7* (31.5) *ab* | 151.5** (9.7) *ab* | 132.7 (6.3) *a* |
| Belview | 44.1 (22.1) *a* | 88.2 (18.9) *a* | 78.7 (9.2) *a* | 67.6 (17.4) *b* |
| Cheekpoint | 39.4* (33.1) *a* | 36.2 (14.2) *b* | 256.3* (107.6) *b* | 157.3 (35.7) *ac* |

**Table 3 continued:**

| | | | | |
|---|---|---|---|---|
| **Monocotyledons** | | | | |
| *Phragmites australis* | | | | |
| Granagh | 20.5 (18.9) | 29.9 (7.9) | 185.8 (70.5) | 158.8 (128.9) |
| *Schoenoplectus tabernaemontani* | | | | |
| Granagh | 17.3 (12.6) *a* | 50.4 (17.3) *a* | 69.5 (112.5) *a* | 86.9 (82.1) *a* |
| Maypark | 56.7 (17.3) *b* | 78.7 (41.0) *a* | 174.2 (21.7) *a* | 278.5** (53.6) *b* |
| *Spartina* spp. | | | | |
| Maypark | 17.3 (12.6) *a* | 25.2 (17.3) *a* | 123.6 (26.5) *a* | 181.5* (47.3) *a* |
| Belview | 113.4 (33.1) *b* | 53.5 (50.4) *a* | 72.4 (9.7) *a* | 96.5* (32.8) *a* |
| Cheekpoint | 52.0 (12.6) *a* | 69.3 (29.9) *a* | 290.5 (107.6) *b* | 517.4** (164.6) *b* |
| *Agrostis stolonifera* | | | | |
| Maypark | 6.3 (6.3) *a* | 138.6* (138.6) *a* | 219.1 (51.2) *a* | 539.6** (399.1) *a* |
| Cheekpoint | 15.8 (14.2) *a* | 22.1 (17.3) *a* | 96.7 (32.8) *b* | 103.8 (57.4) *a* |

< = below limits of detection (Cu 4.7 μmol $kg^{-1}$, Pb 66.1 μmol $kg^{-1}$)

t-test: significant differences in metal concentrations between shoot and root for each plant species. **P = 0.01 *P = 0.05

**Table 4.** Shoot-to-root ratios for Cu and Pb concentrations in plant species at salt marsh sites along the Suir Estuary in 1997. Sediment porewater salinity (g $l^{-1}$) measured at each site in December 1997 is also presented. The number of replications is four.

| | Granagh | Maypark | Belview | Cheekpoint |
|---|---|---|---|---|
| Sediment porewater salinity (g $l^{-1}$) | 8.2 | 12.1 | 16.4 | 20.3 |
| **Cu shoot-to-root ratios** | | | | |
| *Aster tripolium* | 0.2 | 0.6 | 0.8 | 1.6 |
| *Plantago maritima* | -- | 0.4 | 0.5 | 1.1 |
| *Phragmites australis* | 0.7 | -- | -- | -- |
| *Schoenoplectus tabernaemontani* | 0.3 | 0.7 | -- | -- |
| *Spartina* spp. | -- | 0.7 | 2.1 | 0.8 |
| *Agrostis stolonifera* | -- | 0.1 | -- | 0.7 |
| **Pb shoot-to-root ratios** | | | | |
| *Aster tripolium* | 0.0 | 0.0 | 1.2 | 1.5 |
| *Plantago maritima* | | 1.1 | 1.2 | 1.6 |
| *Phragmites australis* | 1.2 | | | |
| *Schoenoplectus tabernaemontani* | 0.8 | 0.6 | | |
| *Spartina* spp. | | 0.7 | 0.8 | 0.6 |
| *Agrostis stolonifera* | | 0.4 | | 0.9 |

## Comparisons between metal concentrations in plants and sediments

Root-to-sediments ratios for Cu and Pb were calculated for each of the species at each of the sites (Table 5). There was a notable increase in the root-to-sediment ratio for Pb in *A. tripolium* between the low salinity site at Granagh and the high salinity site at Cheekpoint although there was a slight reversal in trend in the two mid-estuary sites (Maypark and Belview). No clear trend in root-to-sediment ratios for Cu was recorded in the case of the dicotyledons *A. tripolium* and *P. maritima,* as salinity increased. There was an increase in root-to- sediment

**Table 5.** Root-to-sediment ratios for Cu and Pb concentrations in plant roots and sediment samples taken from between the roots of plant species at salt marsh sites along the Suir Estuary in 1997. Sediment porewater salinity (g $l^{-1}$) measured at each site in December 1997is also presented. The number of replications is four.

| | **Granagh** | **Maypark** | **Belview** | **Cheekpoint** |
|---|---|---|---|---|
| Sediment porewater salinity (g $l^{-1}$) | 8.2 | 12.1 | 16.4 | 20.3 |
| **Cu root-to-sediment ratios** | | | | |
| *Aster tripolium* | 0.2 | 0.4 | 0.6 | 0.3 |
| *Plantago maritima* | | 0.4 | 0.4 | 0.3 |
| *Phragmites australis* | 0.1 | | | |
| *Schoenoplectus tabernaemontani* | 0.1 | 0.3 | | |
| *Spartina* spp. | | 0.2 | 0.3 | 0.5 |
| *Agrostis stolonifera* | | 0.7 | | 0.2 |
| **Pb root-to-sediment ratios** | | | | |
| *Aster tripolium* | 0.3 | 0.5 | 0.4 | 1.7 |
| *Plantago maritima* | | 0.7 | 0.3 | 1.1 |
| *Phragmites australis* | 0.6 | | | |
| *Schoenoplectus tabernaemontani* | 0.3 | 1.0 | | |
| *Spartina* spp. | | 0.9 | 0.5 | 3.8 |
| *Agrostis stolonifera* | | 2.6 | | 0.8 |

ratios for both Cu and Pb in *S. tabernaemontani,* from lower to higher salinities. Root-to-sediment ratios declined with increasing salinity in the case of *Agrostis stolonifera.*

The correlation in metal concentrations between sediment and roots and shoots of *A. tripolium* was confirmed by correlation analysis (Table 6). Highly significant negative correlations ($P < 0.01$) were recorded between Pb concentrations in sediment and both roots and shoots of *A. tripolium.* In the case of Cu, only the shoots of *A. tripolium* showed a significant correlation ($P < 0.01$) with sediment concentrations. Significant negative correlations were also recorded between Pb concentrations in sediment and plant parts of *Spartina* spp.. There was a strong positive correlation for Pb concentrations in the case of *A. stolonifera* ($P < 0.01$), while the roots of *P. maritima* showed a positive correlation with sediment Cu concentrations ($P < 0.05$).

**Table 6.** Pearson product-moment correlation coefficients (r) for correlations between metal concentrations in sediment and in roots and shoots of salt marsh plant species along the Suir Estuary.

| | | | Sediment | |
|---|---|---|---|---|
| | **n** | | **Cu** | **Pb** |
| **Dicotyledons** | | | | |
| *Aster tripolium* | 16 | root | -0.06 | -0.79** |
| | 16 | shoot | -0.63** | -0.77** |
| *Plantago maritima* | 12 | root | 0.56* | -0.40 |
| | 12 | shoot | 0.33 | -0.43 |

**Table 6 continued:**

| | | | | |
|---|---|---|---|---|
| **Monocotyledons** | | | | |
| *Phragmites australis* | 4 | root | 0.45 | 0.45 |
| | 4 | shoot | 0.05 | 0.07 |
| *Schoenoplectus* | 8 | root | -0.49 | -0.81* |
| *tabernaemontani* | 8 | shoot | -0.59 | -0.67 |
| *Spartina* spp. | 12 | root | 0.04 | -0.63** |
| | 12 | shoot | 0.50 | -0.62** |
| *Agrostis stolonifera* | 8 | root | 0.50 | 0.84** |
| | 8 | shoot | -0.38 | 0.87** |

**P < 0.01 *P < 0.05

# DISCUSSION

The very significant correlations between Cu and Pb concentrations in sediment taken from between the roots of salt marsh plant species on the Suir Estuary indicate similar accumulation patterns for both metals. Organic matter content, as measured by loss on ignition (LOI), is a key factor that influences the accumulation of metals in salt marsh sediments (Otte, 1991; Williams *et al.*, 1994a; Caçador *et al.*, 2000). This was confirmed by this study which demonstrated very significant correlations between the organic matter content of saltmarsh sediments and Cu and Pb concentrations. This is in agreement with previous research and reaffirms the metal binding properties of organic matter (Beeftink *et al.*, 1982; Otte *et al.*, 1991, 1993, Doyle & Otte, 1997; Wright &

Otte 1999). There was also good correlation between sediment particle size smaller than 63 μm and concentrations of both metals.

Sediment concentrations of Pb and Cu were generally higher in the upper (Granagh) and mid (Maypark and Belview) Suir Estuary sites compared to the lower estuary site at Cheekpoint. This confirms findings by Neill (1998) who recorded higher metal concentrations in intertidal sediments in the upper Suir Estuary. This indicates that the principal sources of Cu and Pb pollution are in the vicinity of Waterford City, and its industrial sites, which are located in the upper Suir Estuary. There were no known outflows of Cu or Pb pollutants downstream of Waterford City up to the time of this study.

Higher Cu concentrations were recorded in roots, compared with shoots, in all plant species, except *Spartina* spp., which had unusually high leaf concentrations at one site only. Otte *et al.* (1991) and Reboredo (1993) also found consistently higher levels of Cu in the roots of monocotyledons and dicotyledons. The variable results with *Spartina* spp. may have been due to differential waterlogging within sites that affects metal uptake (Huiskes & Nieuwenhuize, 1985; Reboredo, 1993), or may also have been influenced by the mixture of *Spartina* species, with possibly different bioaccumulation capacities, present along the Suir Estuary.

There was a clear partitioning of Pb within the plant in the case of monocotyledons. *Agrostis stolonifera, S. tabernaemontani* and *Spartina* spp. all had much higher concentrations of Pb in the roots. *Phragmites australis* was the only monocot species in which Pb, and Cu, was partitioned fairly evenly between roots and shoots. The dicotyledon, *P. maritima,* accumulated Pb mainly in the shoots. This is in agreement with Rozema *et al.* (1985) and Otte *et al.* (1991) who found a higher accumulation of metals in the shoots of dicotyledons.

The concentration of metals in roots and shoots of *A. tripolium*, however, highlighted some additional factors. At the lower salinity sites Pb accumulated only in the roots, with non-detectable levels in the shoots. At higher salinities there was a marked increase in Pb concentration in the shoots. The increase in Pb concentrations in roots and shoots of *A. tripolium,* (with increasing salinity), was accompanied by a concomitant decrease in soil Pb concentrations. This was demonstrated by higher root-to-sediment ratios for Pb in *A. tripolium* at the higher salinity sites. This was also demonstrated by the strong negative correlations between Pb concentrations in the sediment and concentrations of Pb in the roots and shoots of *A. tripolium*.

Undoubtedly, this is not a simple metal exchange between sediment and plant. *Aster tripolium,* and other salt marsh species, have iron plaques formed on the roots (Otte *et al.*, 1989; Sundby *et al.*, 1998), and this factor, along with other complex physical and chemical factors (Otte, 1991; Williams *et al.*, 1994a; Fletcher *et al.*, 1994; Caçador *et al.*, 2000), affects the uptake of metals. Nevertheless, this study shows that with increasing salinity, the concentration of Pb in *A. tripolium* increases, and there is a direct gradient in metal concentrations from the rhizosphere to roots to the aerial parts of the plant. These findings are in general agreement with Otte (1991) who found increased concentrations of metals in most plant parts under saline conditions. He speculated that this may be related to higher mobility of metals in the sediment and/or higher water uptake, (due to increased transpiration), leading to a higher flux of metals into the plant.

There was also an inverse relationship between Pb concentrations in sediment and plant parts of *Spartina* spp.. The highest concentrations of Pb in the roots and shoots of *Spartina* spp. were recorded at the high salinity site at Cheekpoint. Higher concentrations of Pb were recorded in the roots of *Spartina* spp., compared to shoots, regardless of salinity levels. Pb concentrations in *A. stolonifera* differed from all other species in the study. The concentration of Pb in roots and shoots in this species actually decreased along with sediment concentrations. The reasons for this are unclear though large intra-site variation in metal concentrations in *A. stolonifera* was recorded.

There were no clear differences between monocotyledons and dicotyledons in the uptake and translocation of Cu. As in the case of Pb, Cu concentrations were higher in the roots of *A. tripolium* at lower salinities. At higher salinities, however, there was no trend toward higher Cu concentration in the shoots. These findings are in agreement with Otte (1991) who found that salinity treatment did not affect the Cu content of plants and that the metal was mainly stored in the roots. However, in this study, there was also a significant inverse correlation between Cu concentrations in sediment and in *A. tripolium* shoots (with increasing salinity). This would seem to indicate that *A. tripolium* does translocate increasing increments of Cu to aerial parts as salinity increases. However, the rate of respiration in roots as well as shoots also increases with increasing salinity (Marschner, 1995) and this may result in a more even distribution of essential elements, such as Cu, between roots and shoots.

The root/sediment ratios were notably higher for Pb, compared with Cu, for all plant species. When inter-site comparisons are made, in the case of *A. tripolium* for example, it is clear that sites with higher sediment concentrations of Pb had lower root/sediment ratios. This is in agreement with Otte *et al.*, (1991), who found that an increase in soil concentrations of a metal will not lead to a proportional increase in the concentration of that metal in the plant.

The highest root/sediment ratios for Pb were recorded in the case of *Spartina* spp. and *A. stolonifera* but the variation in ratios was large for both species as a result of large intra-site variation in plant metal concentrations. As stated earlier, this may have been due to differential waterlogging within the sites, and additionally, in the case of *Spartina,* to the coexistence of a number of species.

A number of salt marsh species, *A. tripolium* in particular, are used for biomonitoring purposes due to the bioaccumulation of metals in plant tissue. Care needs to be taken when using these plants because this study confirms that there are differences in the way that Cu and Pb are accumulated. Cu is accumulated mainly in the roots of monocotyledons and dicotyledons. Monocotyledons also accumulate Pb mainly in the roots but dicotyledons tend to accumulate Pb in the shoots. This study also confirmed that there is a general trend toward increased shoot/root ratio for Pb in dicotyledons as salinity increases and this was particularly notable in the case of *A. tripolium.* These factors need to be taken into account when choosing salt marsh species for biomonitoring and particular note should be taken of the differences between monocotyledons and dicotyledons. Whole plant samples should be taken but shoots and roots should be analysed separately for metal concentrations.

# CHAPTER 7

# A comparison of copper, lead, and chromium concentrations in seaweed species on the Suir Estuary

## SUMMARY

Concentrations of Cu, Pb and Cr were determined in older thallus parts of three brown (Phaeophyta) seaweed species, *Fucus vesiculosus, F. serratus* and *Ascophyllum nodosum*; and one red (Rhodophyta) seaweed species, *Polysiphonia lanosa*, at five sites along the Suir Estuary in December 1998. Cu concentrations in *F. vesiculosus* ranged from 5.0 – 10.0 mg $kg^{-1}$ while a mean concentration of 8.4 mg $kg^{-1}$ was recorded in *F. serratus* at one site. Cu concentrations in *P. lanosa* ranged from 7.1 – 13.5 mg $kg^{-1}$ and were significantly higher at nearly all sites than its basiphyte, *A. nodosum*. Pb concentrations in the Suir Estuary were very high, even when compared to heavily industrialised sites in Ireland, Britain and mainland Europe. The highest Pb concentrations (34.7 mg $kg^{-1}$) were recorded in *F. vesiculosus* at the mouth of Johns River and these indicated a substantive pollution source in that tributary. Pb concentrations in *P. lanosa* ranged from 19.7 – 24.0 mg $kg^{-1}$ but were not significantly different from that recorded in *A. nodosum*. Cr concentrations were below limits of detection in all seaweed species analyzed. Samples of Suir Estuary water were also taken in December 1998 and analysed for Cu, Pb and Cr concentrations. There were large intra-site variations in water concentrations of all the metals, but especially Pb, and concentrations ranged from 8.0 – 29.9 µg $L^{-1}$. Cu and Cr concentrations in water were generally low. Concentration factors were calculated for the metals in the seaweed species. For *P. lanosa* the concentration factors were 1.4 x $10^3$ for Cu and these were significantly higher than for *A. nodosum*. There were no significant differences between species in concentration factors for Pb, which ranged from 0.8 – 1.2 x $10^3$. *Polysiphonia lanosa,* compared with other species, generally contained the highest concentration of Cu and Pb at each of the sites

and had the lowest intra-site variation. *Polysiphonia lanosa* is proposed as an alternative to *F. vesiculosus* and *A. nodosum* for biomonitoring of metals in estuaries. It is also proposed that research be carried out into the potential of *P. lanosa* as a biofiltration agent for the removal of metals from waste streams.

## INTRODUCTION

Seaweed species, in particular brown macroalgae (Phaeophyta), have been widely used for biomonitoring of metal contaminants in estuarine environments. The most commonly used species are *Fucus vesiculosus, Fucus serratus, Ascophyllum nodosum* and *Laminaria digitata* (Bryan & Hummerstone, 1973; Eide & Myklestad, 1980; Barnett & Ashcroft, 1985; Forsberg *et al.*,1988; Molloy & Hills, 1996; O'Leary & Breen, 1997, 1998; Stengel & Dring, 2000). *Polysiphonia lanosa*, a red macroalga (Rhodophyta) which is hemiparasitic on *A. nodosum,* has not been investigated in any detail for metal bioaccumulation, although Munda (1982) recorded its sensitivity to organic pollution and Crist *et al.* (1992) investigated the basic chemistry of metal adsorption in *P. lanosa*. Where seaweed species have been compared for uptake of metals, concentrations have been higher in *F. vesiculosus* than in *A. nodosum* (Foster, 1976; Ho, 1984; Riget *et al.*, 1997). A limited number of comparative studies (Fuge & James, 1973; Tomlinson *et al.* 1980) have reported no significant differences in metal levels in *F. vesiculosus* and *F. serratus* collected from similar positions on the shore.

Some seaweed species take up metals from the surrounding waters (Foster, 1976) though research by Luoma *et al.* (1982) indicated that scavenging of metals from particulates may be an important source of uptake by seaweeds. Phillips (1977) cautioned against trying to correlate the concentrations of metals in seaweed tissue and seawater because of the extraneous effects of water sampling and environmental variables such as salinity, turbidity and water temperature. However, other researchers (Morris & Bale, 1975; Seeliger & Edwards, 1977) did find good agreement between concentrations of metals in water and *F. vesiculosus*. Leal *et al*., (1997) recorded good agreement between mean metal concentration factors at three sites on the Oporto coast from eight monthly samplings of each medium. Seaweeds integrate short-term temporal fluctuations in concentrations and older parts of the thallus are more retentive of metals (Bryan & Hummerstone, 1973; Phillips, 1994). More recent research has found the patterns of accumulation to be similar between different-aged thallus parts for Cu and Pb in *F. vesiculosus* (Forsberg *et al*., 1988; Carvalho *et al*., 1996). Seasonal variation of metals in brown seaweeds has been noted by several researchers (Fuge & James, 1974; Miramand & Bentley, 1992; Stengel & Dring, 2000), and they concluded that maximum concentrations of metals were found in winter. Leal *et al*. (1997) recorded the highest concentrations of Cu and Pb in *Enteromorpha* spp. and *Porphyra* spp. in spring. However, Eide *et al*. (1980) and Riget *et al*. (1995) found that Pb uptake by seaweed species appeared to be largely independent of seasonal factors.

The aims and expected outcomes of this study were:

(a) To compare three brown (Phaeophyta) seaweed species, *F. vesiculosus, F. serratus* and *A. nodosum* and one red (Rhodophyta) seaweed species, *P.*

*lanosa*, for accumulation of Cu, Pb and Cr on the Suir estuary. Differences in metal concentrations were expected between seaweed species due to differences in bioaccumulation capacities.

(b) To compare the metal concentrations in the seaweed species with estuary water concentrations and examine if there is any correlation. Low correlation between metal concentrations in seaweeds and estuary water was expected due to short-term fluctuations in water pollution concentrations and longer term bioaccumulation in seaweeds.

(c) To determine if the seaweed species can be used for biomonitoring of metal pollution. The three Fucoid species, *F. vesiculosus, F. serratus* and *A. nodosum* are already commonly used for biomonitoring but, to-date, only limited research has been carried out with *P. lanosa.*

## MATERIALS AND METHODS

### Site

Five study sites were identified on the Suir Estuary (Figure 1), extending from the mouth of Johns River, a minor tributary that flows through Waterford City, to Passage East (Table 1).

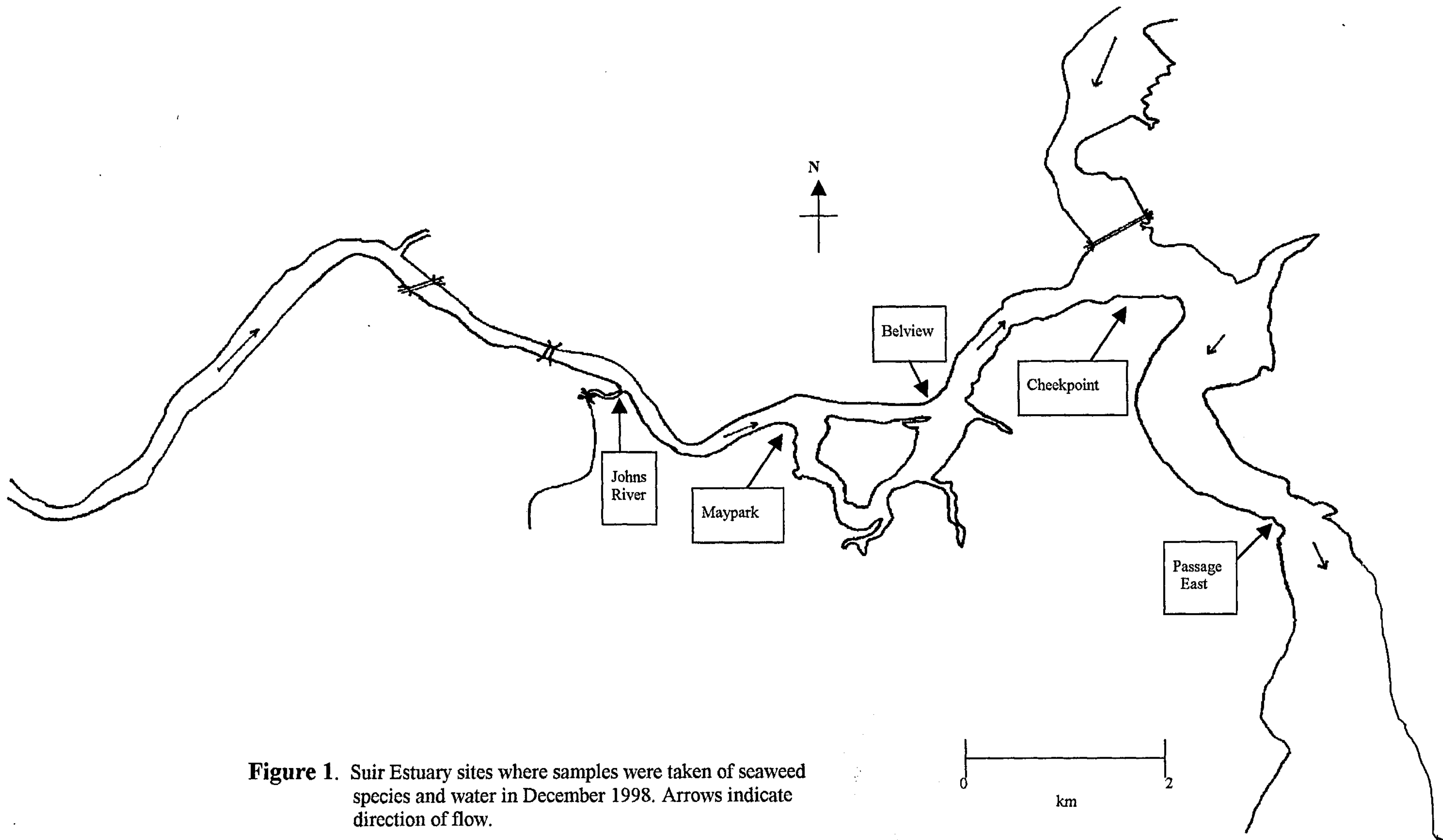



**Figure 1**. Suir Estuary sites where samples were taken of seaweed species and water in December 1998. Arrows indicate direction of flow.

**Table 1.** Location of sites where samples of seaweed species and water were collected in December 1998.

| site | coordinates* | seaweed species | | | | water |
|---|---|---|---|---|---|---|
| | | *F. vesiculosus* | *A. nodosum* | *P. lanosa* | *F. serratus* | |
| Johns River | S 614 124 | + | | | | + |
| Maypark | S 635 118 | + | | | | + |
| Belview | S 654 122 | + | + | + | | + |
| Cheekpoint | S 683 137 | + | + | + | | + |
| Passage East | S 701 103 | + | + | + | + | + |

* Ordnance Survey of Ireland: 1/50,000 Discovery Series, number 76

## Analysis of seaweed material

*Sampling and pretreatment of seaweed species*

Sampling of seaweed species was carried out at the five sites on 14-16$^{th}$ December 1998. Four specimens of each species were collected at each site and mature parts of the thalli were cut from full-size specimens according to the method outlined in Chapter 3.

*Determination of Cu, Pb and Cr concentrations*

See Chapter 3 for details of metal analysis of seaweed species.

**Sampling and analysis of estuary water**

*Sampling*

Four 250 ml water samples were taken in HDPE bottles from the surface of the Suir estuary, at each of the five sites, on 7-8$^{th}$ December 1998.

Temperature and pH readings were taken of the estuary water at each site at the time of sampling. Salinity measurements were taken at the laboratory according to the method outlined in Chapter 3.

*Determination of Cu, Pb and Cr concentrations*

See Chapter 3 for details of metal analysis of estuary water.

## RESULTS

**Metal concentrations in seaweed species**

Cu concentrations in *F. vesiculosus* ranged from 5.0 – 10.0 mg kg$^{-1}$ while a mean concentration of 8.4 mg kg$^{-1}$ was recorded in *F. serratus* at the Passage East site (Table 2). Cu concentrations in *P. lanosa* ranged from 7.1 – 13.5 mg kg$^{-1}$ and were significantly higher at nearly all sites than its basiphyte, *A nodosum*. Pb concentrations in *F. vesiculosus* ranged from 10.5 mg kg$^{-1}$ at Belview to a peak of 34.7 mg kg$^{-1}$ at Johns River. Pb concentrations in *P. lanosa* ranged from 17.5 – 24.0 mg kg$^{-1}$ but were not significantly different from *A. nodosum*. Cr concentrations were below limits of detection in all seaweed species.

**Table 2.** Mean Cu, Pb and Cr concentrations (mg $kg^{-1}$ dry weight) in seaweed species from sites on the Suir estuary in December 1998. Standard deviations are shown in brackets. The number of replications is four. Values with different letters within a column per metal per seaweed species are significantly different (Tukey test).

| | Johns River | Maypark | Belview | Cheekpoint | Passage East |
|---|---|---|---|---|---|
| **Cu** | | | | | |
| *F. vesiculosus* | 9.6 (0.7) | 5.6 (1.0) *a* | 5.5 (1.4) *ab* | 5.0 (1.1) *a* | 10.0 (10.7) *a* |
| *A. nodosum* | - | 4.5 (1.3) *a* | 4.1 (1.1) *a* | 3.9 (0.4) *a* | 5.4 (1.6) *a* |
| *P. lanosa* | - | 9.6 (0.9) *b* | 7.1 (0.5) *b* | 8.3 (0.9) *b* | 13.5 (1.9) *a* |
| *F. serratus* | - | - | - | - | 8.4 (1.5) *a* |
| **Pb** | | | | | |
| *F. vesiculosus* | 34.7 (2.9) | 21.6 (2.2) *a* | < | < | < |
| *A. nodosum* | - | 17.8 (0.9) *a* | 18.6 (3.1) *a* | < | < |
| *P. lanosa* | - | 24.0 (6.9) *a* | 23.3 (2.6) *a* | < | 19.7 (3.7) *a* |
| *F. serratus* | - | - | - | - | 18.6 (2.3) *a* |
| **Cr** | | | | | |
| *F. vesiculosus* | < | < | < | < | < |
| *A. nodosum* | - | < | < | < | < |
| *P. lanosa* | - | < | < | < | < |
| *F. serratus* | - | - | - | - | < |

< = below limits of detection (Cu 0.7 mg $kg^{-1}$, Pb 17.7 mg $kg^{-1}$, Cr 6.5 mg $kg^{-1}$, dry weight)

- not relevant

Two-way analysis of variance showed that there were significant differences in metal concentrations between sites and between seaweed species (Table 3).

**Table 3.** Results of two-way analysis of variance for differences in Cu, Pb and Cr concentrations between sites and between seaweed species.

| | Between species | Between sites | Interaction |
|---|---|---|---|
| Cu | *** | * | *** |
| Pb | n.s. | *** | *** |
| Cr | - | - | - |

n.s. = not significant - not relevant

***P < 0.001 *P < 0.05

**Metal concentrations in water and seaweed species**

Pb concentrations in Suir Estuary water were higher, but much more variable than the other metals, and ranged from 8.0 – 29.9 μg $l^{-1}$ (Table 4). A single elevated concentration of 17.4 μg $l^{-1}$ of Cr was recorded at the Maypark site but concentrations at other sites were low. A gradual increase in Cu concentrations was recorded at the downstream sites. There was a significant correlation (P<0.05) between Cu and salinity levels in water (Table 5). There were no significant correlations between metal concentrations in water and concentrations in any of the seaweed species (Table 6).

**Table 4.** Mean Cu, Pb and Cr concentrations ($\mu g\ l^{-1}$) in Suir estuary surface water from samples collected in December 1998. Standard deviations are shown in brackets. Values with different letters within a column per metal per site are significantly different (Tukey test). The number of replications is four.

| **site** | **Cu** | **Pb** | **Cr** |
|---|---|---|---|
| Johns River | < | 14.2 (2.1) *a* | 6.0 (5.9) *a* |
| Maypark | 5.4 (2.0) *a* | 28.8 (21.2) *a* | 17.4 (6.2) *b* |
| Belview | 7.4 (2.3) *ab* | 9.4 (1.7) *a* | < |
| Cheekpoint | 9.2 (2.5) *ab* | 29.9 (28.5) *a* | 3.9 (1.7) *a* |
| Passage East | 11.0 (3.5) *b* | 8.0 (7.1) *a* | 4.4 (1.1) *a* |

< = below limits of detection (Cu 2.5 $\mu g\ l^{-1}$, Pb 1.3 $\mu g\ l^{-1}$, Cr 3.1 $\mu g\ l^{-1}$).

**Table 5.** Product Moment Correlation Coefficient (r) between salinity and Cu, Pb and Cr concentrations in Suir Estuary water. n = 20.

| | **Cu** | **Pb** | **Cr** |
|---|---|---|---|
| **water salinity** | + 0.47* | + 0.27 | + 0.36 |

*P < 0.05

**Table 6.** Product Moment Correlation Coefficients (r) for Cu, Pb and Cr concentrations in estuary water and seaweed species along the Suir Estuary.

| | n | Cu water | Pb water | Cr water |
|---|---|---|---|---|
| *Fucus vesiculosus* | 20 | 0.35 | 0.00 | - |
| *Ascophyllum nodosum* | 16 | 0.00 | 0.25 | - |
| *Polysiphonia lanosa* | 16 | 0.36 | 0.22 | - |

\- not relevant

Concentration factors for each of the metals were calculated by dividing the mean concentrations of the metals in the seaweed species by the mean metal concentrations in water. Concentration factors for *P. lanosa* were $1.4 \times 10^3$ for Cu and these were significantly higher than for *A. nodosum* (Table 7). There were no significant differences between species in concentration factors for Pb.

**Table 7.** Concentration factors for Cu, Pb and Cr in seaweed species (mg $kg^{-1}$ dry weight seaweed per μg $l^{-1}$ estuary water). Values with different letters within a column are significantly different (Tukey test).

| | n | Cu | Pb | Cr |
|---|---|---|---|---|
| *F. vesiculosus* | 20 | $0.9 \times 10^3$ *ab* | $0.8 \times 10^3$ *a* | - |
| *A. nodosum* | 16 | $0.6 \times 10^3$ *a* | $1.0 \times 10^3$ *a* | - |
| *P. lanosa* | 16 | $1.4 \times 10^3$ *b* | $1.2 \times 10^3$ *a* | - |

\- not relevant

**Table 8.** Mean concentrations of metals (mg kg$^{-1}$ dry weight) in seaweed species in Irish and other European estuaries.

| ***Fucus vesiculosus*** | **Cu** | **Pb** | **Cr** | |
|---|---|---|---|---|
| Suir Estuary | 7.1 | 19.0 | < | this study[1] |
| East Ireland (baseline) | 3.8 | 1.3 | - | Tomlinson *et al.* (1980)[2] |
| Carnsore Point | 6.9 | - | - | Cullinane & Whelan (1982)[2] |
| Dungarvan | 7.0 | - | - | Cullinane & Whelan (1982)[2] |
| Shannon (Bunaclugga Bay) | 10.0 | - | 35.0 | O'Leary & Breen (1998)[3] |
| Cork Harbour (Monkstown) | 14.2 | - | - | Cullinane & Whelan (1982)[2] |
| Humber (South Bank) | 42.6 | 8.1 | - | Barnett & Ashcroft (1985)[1] |
| Mersey Estuary | 28.0 | 10.9 | 3.7 | Langston (1986)[2] |
| Tagus Estuary (Portugal) | 37.0 | 18.0 | - | Carvalho *et al.* (1997)[1] |

| ***Fucus serratus*** | **Cu** | **Pb** | **Cr** | |
|---|---|---|---|---|
| Suir Estuary | 8.4 | 18.6 | < | this study[1] |
| Severn Estuary (Sand Point) | 14.3 | 6.4 | - | Martin *et al.* (1997)[1] |
| Goury (NW France) | 1.1 | 1.1 | 0.2 | Miramand & Bentley (1992)[2] |

| ***Ascophyllum nodosum*** | **Cu** | **Pb** | **Cr** | |
|---|---|---|---|---|
| Suir Estuary | 4.5 | 17.2 | < | this study[1] |
| Carnsore Point | 3.5 | - | - | Cullinane & Whelan (1982)[2] |
| Cork Harbour (Monkstown) | 10.9 | - | - | Cullinane & Whelan (1982)[2] |
| Clyde Estuary (Hunterston) | 20.0 | 4.0 | - | Molloy & Hills (1996)[2] |

| ***Polysiphonia lanosa*** | **Cu** | **Pb** | **Cr** | |
|---|---|---|---|---|
| Suir Estuary | 9.6 | 21.1 | < | this study[2] |

[1] mature thallus [2] whole plant [3] frond tips

< = below limits of detection - not relevant

## DISCUSSION

Metal concentrations in seaweed species on the Suir Estuary were compared with previous studies elsewhere in Ireland and Europe (Table 8). Cu concentrations in all seaweed species in the Suir Estuary were above baseline levels (3.8 mg $kg^{-1}$) for the east coast of Ireland, as proposed by Tomlinson *et al.* (1980). Cu concentrations in the Suir Estuary (range 5.0 – 10.0 mg $kg^{-1}$ in *F. vesiculosus*) were very similar to those recorded by Cullinane & Whelan (1982) in *F. vesiculosus* and *A. nodosum* along the south coast of Ireland. However, Cu concentrations in *F. vesiculosus* in the Suir Estuary were lower than those recorded by Cullinane & Whelan (1982) in Cork Harbour and by O'Leary & Breen (1998) in the Shannon Estuary. Overall, Cu levels in seaweed species were low when compared with heavily industrialized sites in Britain and elsewhere in Europe. Cr concentrations were below limits of detection (LOD) in all seaweed species.

In contrast, Pb concentrations in all the seaweed species in the Suir Estuary were very high, even in comparison with heavily industrialised areas of Britain and mainland Europe. Pb concentrations in *F. vesiculosus* in the Suir Estuary (range 17.8 - 34.7 mg $kg^{-1}$) were higher than those recorded by Barnett & Ashcroft (1985) in the Humber and by Langston (1986) in the Mersey Estuary. The Pb concentrations in *F. vesiculosus* in the Suir Estuary were also higher than those recorded in the Tagus Estuary, which is heavily polluted by ship building and smelting industries (Carvalho *et al.*, 1997). The high concentrations of Pb (34.7 mg $kg^{-1}$) recorded in *F. vesiculosus* at Johns River were probably of anthropogenic origin. This indicates high levels of Pb pollution getting into Johns River, from one or more sources, and being transported into the Suir estuary.

*Polysiphonia lanosa* contained high concentrations of metals compared to the other seaweed species. It contained significantly higher levels of Cu (7.1 - 13.5 mg $kg^{-1}$) than its basiphyte, *A. nodosum* (3.9 – 5.4 mg $kg^{-1}$) at Maypark and Cheekpoint. *Polysiphonia lanosa* also contained significantly higher concentrations of Cu and Pb than *F. vesiculosus* at Belview, Cheekpoint and Passage East. The higher concentration of metals in *P. lanosa* may be at least partly due to its polysiphonous morphology (Kumar & Singh, 1979) that results in a very large surface area-to-mass ratio. This is likely to enhance the absorptive properties of this species. *Polysiphonia lanosa*, a Rhodophyte, belongs to a different phylogenetic group to the Fucoid species and there are differences between the two groups in the structures involved in the transport of nutrients (Penot *et al.*, 1993). This is likely to have implications also for differences in metal uptake and translocation between the seaweed groups. Penot *et al.*, (1993) have demonstrated that the transport of phosphorus from *A. nodosum* to *P. lanosa* is uni-directional and could explain, in part at least, how the concentration of P was four times higher in *P. lanosa* than in *A. nodosum*. However, further research is required to investigate the dynamics of metal uptake by *P. lanosa* and *A. nodosum* and what influence the host-hemiparasite relationship might have on this uptake.

*Fucus vesiculosus* did not accumulate significantly higher concentrations of metals than *A. nodosum,* which appears to disagree with earlier studies that recorded higher uptake by *F. vesiculosus* (Foster, 1976; Ho, 1984). However, Riget *et al.* (1997) also found no significant difference in Pb and Cr concentrations between these species. Metal concentrations in *F. serratus* were similar to those in *F. vesiculosus,* which is in agreement with Tomlinson *et al.* (1980), but comparisons were limited to one site only in this study.

The mechanism by which the seaweeds detoxify metals and bind them within the cells resulting in a complex which can either be stored in compartments within the cell or excluded to the surrounding environment is poorly understood. Work carried out by Smith *et al.* (1986) suggested that the metal was localised in the physodes of the photosynthetic cells. Toth & Pavia (2000) demonstrated that the production of phlorotannins, which are found in physodes and which are strong chelators of metals in solution, did not increase in response to high Cu concentrations. Other suggestions for mechanisms of metal binding are by complexation with polyphenols (Ragan *et al.*, 1979), synthesis of phytochelatin complexes (Gekeler *et al.*, 1988), or algal metallothioneins (Robinson, 1989).

The concentration of Cu in water increased with increasing salinity, which confirms work by other researchers (Mantoura *et al.*, 1978; Liu *et al.*, 1998), who found that the concentration of $Cu^{2+}$ rises with increasing salinity. $Cu^{2+}$ is the most bioavailable copper ion and increasing concentration in more saline water may occur because the binding of Cu to humics is decreased due to competition from $Ca^{2+}$ and $Mg^{2+}$. The concentrations of Pb and Cr in water did not correlate with salinity.

Research has shown that maximum concentrations of metals are present in seaweed species during winter and spring when frond growth is at its lowest and, as a consequence, dilution of metal concentrations by new tissue is also at its lowest (Fuge & James, 1974; Miramand & Bentley, 1992; Leal *et al.*, 1997; Martin *et al.*, 1997; Stengel & Dring, 2000). For this reason sampling of seaweed species in this study was carried out in December.

Sampling of seaweed species and water in this study was not carried out on the same day at each of the sites, although both sets of samples were taken within a week of each other. This divergence in time of sampling undoubtedly contributed to the low level of correlation between metal concentrations in water and seaweed species recorded in this study. The poor correlation is in agreement with Phillips (1977) who pointed out the extraneous effects of water sampling and of a range of environmental variables including salinity, turbidity and temperature. Leal *et al.* (1997) found marked variation in metal concentrations in *Enteromorpha* spp. and *Porphyra* spp. from month to month and concluded that metal concentration factors (alga/water) based on single or few determinations could be misleading. Their study showed that the mean concentration factors (mean metal concentration in the alga divided by the mean metal concentration in water over an eight month period) were relatively constant and they concluded that algae could be used to estimate the mean concentrations of a number of metals in water, including Cu and Pb. However, Leal *et al.* (1997) also concluded that because sampling and analysis of the algae was carried out on a monthly basis over an eight-month period, that the use of algae as biomonitors of metal pollution could have little practical advantage over the direct analysis of metals in seawater. However, water is subject to daily or even hourly fluctuations in metal concentrations, depending on pollution inputs (Phillips, 1977) and water volume flows, and this study has shown that intra-site variation can be very high even in the case of water samples taken within minutes of each other. Add to this the difficulties of analyzing metals in saline water due to low concentrations and interference from salt ions, particularly in the case of Pb (Chapter 3).

Concentration factors of approximately $10^3$ were recorded for Cu and Pb in the seaweed species on the Suir Estuary. These are at the lower end of the range ($10^3$ – $10^5$) as reviewed by Phillips (1994). *Polysiphonia lanosa* had higher concentration factors for Cu than its host, *A. nodosum*, confirming the higher level of uptake by the hemiparasite. There was no significant difference in concentration factors between *P. lanosa* and *F. vesiculosus* for Cu. The large fluctuations, and intra-site variances of Pb concentrations in water were probably the main reasons why there were no significant differences between species in concentration factors for that metal.

This study confirmed the difficulties of trying to make a direct comparison between metal concentrations in estuary water and seaweed species. Metal concentrations in water are subject to transitory fluctuations and large intra-site variations due to the extraneous effects of water sampling and a range of environmental factors. Seaweed species, on the other hand, integrate short-term temporal fluctuations and give a more even, concentrated measure of long-term pollution (Phillips, 1994). Another important advantage to using seaweed species for monitoring metal pollution compared to non-biotic media (e.g. sediments) is that metal concentrations in seaweed tissue reflect the availability of particular pollutant chemicals in the water medium for uptake by biota (Bryan *et al.*, 1985). The relatively high concentrations of Pb recorded in the four seaweed species in this study could have implications for other biota in the food chain of the Suir Estuary in the longer term (Miramand & Bentley, 1992; Williams *et al.*, 1994a; Wright & Mason 1999).

Seaweeds are valuable biotic tools for comparison of metal pollution between sites, between estuaries, and between years. Multiple samplings and analyses of seaweed species, preferably on a monthly basis, are recommended. However, this may not be possible due to economic and resource limitations. As many monthly samplings as possible should be taken during winter and spring when maximum metal concentrations are present in seaweed species.

*Polysiphonia lanosa* contained high concentrations of Cu and Pb compared to the other seaweed species in this study and the intra-site variation was low. *Polysiphonia lanosa* can be proposed as an alternative, or addition, to *F. vesiculosus* and *A. nodosum* for biomonitoring of metals in estuaries primarily because of the low intra-site variation. It is also proposed that research be carried out into the potential of *P. lanosa* as a biofiltration agent for the removal of metals from waste streams because of its relatively high bioaccumulation potential.

# General Discussion

Within an estuary there are four main compartments that interrelate actively with each other (Figure 1). The movement of pollutants, including heavy metals, between these compartments is of major significance in the overall environmental status of an estuary. The movement of metals in an estuary is influenced by a complex range of physico-chemical and biogeochemical factors that are outlined in Figure 1. Metal contamination of estuaries can occur from atmospheric deposition (Clark, 1989; Fletcher *et al.*, 1994), but the only likely source for atmospheric pollution of the three metals in this study (Cu, Pb, Cr) on the Suir Estuary, was Pb halide emissions from automobiles. The significance of this atmospheric Pb contamination in the Suir Estuary is not known but the high concentrations of Pb in the midlittoral sediments (63.4 mg $kg^{-1}$) and in *F. vesiculosus* (34.7 mg $kg^{-1}$) at Johns River are a strong indication of point rather than diffuse sources (Chapter 5 and Chapter 6). This research focused primarily on the other three compartments; biota (salt marsh vegetation and seaweed species), sediments and water.

The primary pathway for metal movement within an estuary is water. As the majority of metals, including Cu, Pb and Cr, are discharged into estuaries they tend to become bound to suspended particulate material in the water column (Mantoura *et al.*, 1978; Loring & Prosi, 1986; Bubb & Lester, 1991). The particulate matter, with its metal load, then rapidly settles in the sediments (McLuskey, 1989; Paucot & Wollast, 1997; Liu *et al.*, 1998). The metals can be

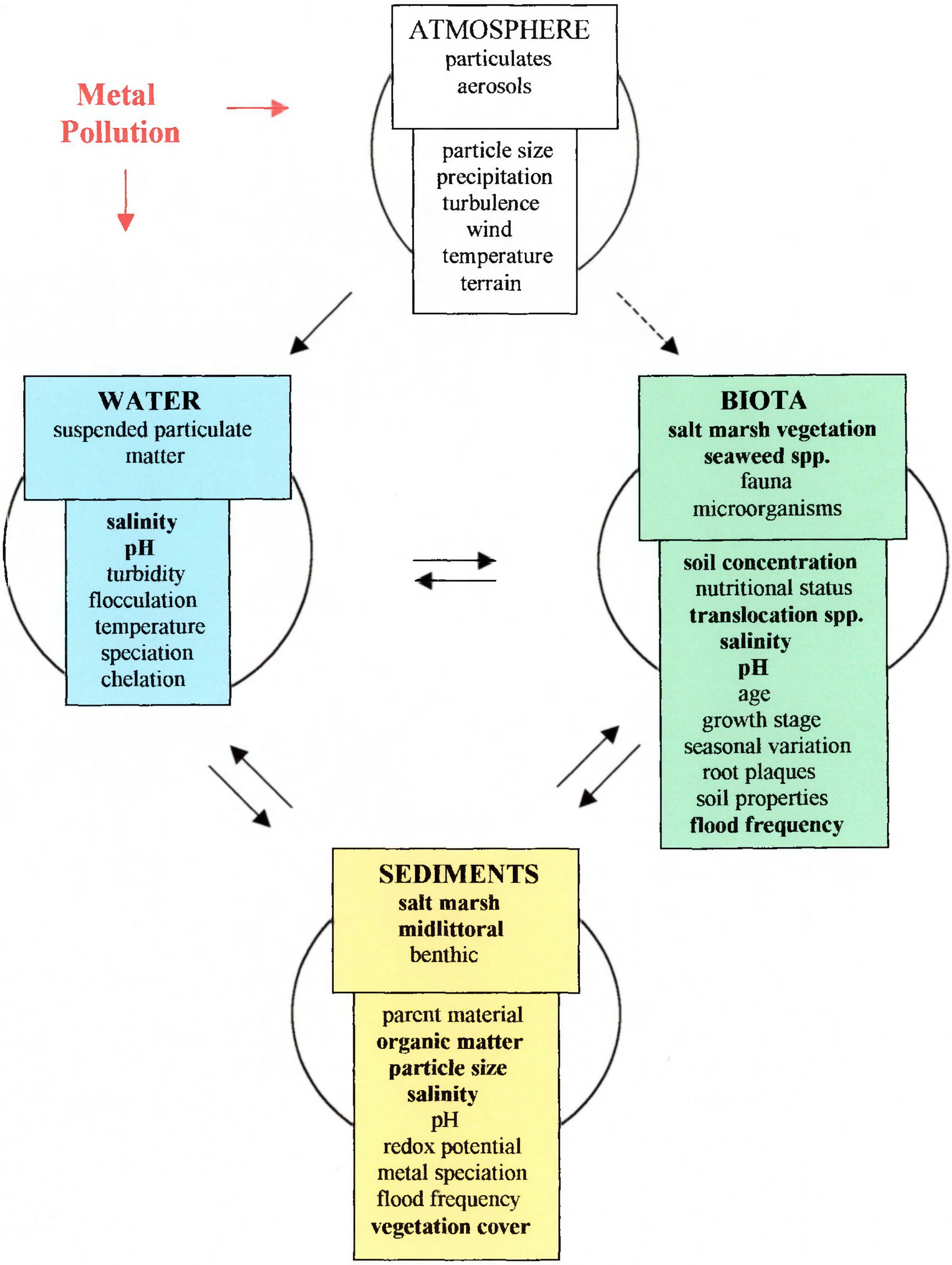



**Figure 1**. Schematic model of movement of metals and associated factors within an estuary. Upper boxes signify compartments, lower boxes signify factors that influence the movement of metals. Bold letters indicate compartments and factors that were investigated in this study.

remobilized by physical disturbances from tidal action, storms, boat traffic, dredging and bioturbation (Fletcher *et al.*, 1994).

The metal concentration data recorded from the various compartments in the Suir Estuary is summarized in Figure 2. There was a significant downward trend from the upper to the lower Suir Estuary in midlittoral sediment concentrations of Cu, Pb and Cr probably as a result of anthropogenic pollution sources in the upper estuary but also because of dilution of contaminated sediments with relatively clean marine sediments further downstream (Attrill & Thomes, 1995; Zwolsman *et al.*, 1996; Chapter 5). The presence of Pb pollution in the upper estuary was further supported by high concentrations of Pb (34.7 mg $kg^{-1}$) in *F. vesiculosus* at the mouth of Johns River. The higher concentrations of Cr at the upper estuary sites (42.8 mg $kg^{-1}$ at Granagh) are probably a result of historical pollution from old tanneries further upstream. Another factor influencing the decrease in metal concentrations downstream could be the release of metals to the water column as the freshwater and seawater mix (Wright & Mason, 1999). This study (Chapter 7) showed that the concentration of Cu in water increased with increasing salinity, i.e. downstream. This may be because the binding of Cu to sediment is decreased due to competition from $Ca^{2+}$ and $Mg^{2+}$.

There were no differences in metal concentrations between midlittoral sediments and salt marsh sediments taken from between the roots of *A. tripolium* in the Suir Estuary (Chapter 5). This appears to conflict with previous research by Fletcher *et al.* (1994) and Wright & Mason (1999) who found generally higher concentrations of metal in salt marsh sediments compared to midlittoral sediments. Organic matter is one of the key factors that affect the ability of sediments to retain metal ions (Elliott *et al.*, 1986; Otte *et al.*, 1991, 1993; Williams *et al.*, 1994b; Harland *et al.*, 2000). The organic matter contents of the midlittoral and salt marsh sediments in this study were surprisingly similar (Chapter 5) and this may be the reason for the similarity in metal concentrations. The salt marsh sediment samples were taken from between the roots of *A. tripolium*, a halophyte normally found in the lower salt marsh zone while the midlittoral samples were taken midway along the midlittoral zone. Perhaps the pattern of organic matter accumulation for both sediments is similar as they are situated relatively closely to each other, but further investigation is needed.

The dominant uptake pathway for most salt marsh plants is via the root system, with subsequent acropetal translocation from the root to the aerial parts (Rozema *et al.*, 1988). Consequently most metals tend to accumulate in the roots rather than in leaves or shoots. In this study the highest concentrations of Pb were recorded in the roots of monocotyledons while dicotyledons contained the highest concentrations of Pb in the shoots (Chapter 6). However, higher Cu concentrations were recorded in the roots of all monocotyledons and dicotyledons examined, except *Spartina* spp.. These findings are in general agreement with other researchers (Rozema *et al.*, 1985; Otte *et al.*, 1991; Reboredo, 1993). The mixed results with *Spartina* spp. may be due to the coexistence of a number of species along the Suir estuary or they may also be due to differential waterlogging within sites that influences the uptake of metals (Huiskes & Nieuwenhuize 1985; Reboredo, 1993).

In estuaries, salinity is one of the most important factors governing salt marsh zonation (Rozema *et al.*, 1985). As salinity increases, flood tolerance decreases (Beeftink, 1985; Chapter 3). Salinity reduces the growth rates of many halophytes including *A. tripolium, S. anglica* and *E. atherica* (Rozema *et al.*, 1985, 1990; Chapter 3). Salinity is also a key factor in the translocation of metals from roots to shoots in *Aster tripolium* (Otte, 1991; Chapter 6). This study showed that with increasing salinity, the uptake of Pb from the soil by *A. tripolium* increases and there is a direct gradient in metal concentration from the roots to aerial parts of the plant. At low salinity sites Pb accumulated only in the roots whereas at higher salinity sites there was a marked translocation to the leaves. Otte (1991) speculated that this may be related to higher mobility of metals in the soil at higher salinity, and/or higher water uptake, (due to increased transpiration), leading to a higher flux of metals into the plant.

At higher salinities, however, Cu concentrations in the shoots were not significantly higher than root concentrations (Chapter 6). But there was a significant inverse correlation between Cu concentrations in the soil and *A. tripolium* shoots, as salinity increased. This would seem to indicate that *A. tripolium* does translocate increasing increments of Cu from the sediment to aerial parts, as salinity increases. However, the rate of respiration in roots as well as shoots also increases with increasing salinity (Marschner, 1995), and this may result in a more even distribution of essential elements, such as Cu, between roots and shoots.

Most seaweed species take up metals directly from the surrounding waters (Foster, 1976) though scavenging of metals from particulate matter may also be an important source of uptake (Luoma *et al.*, 1982). Metal concentrations in seaweed species on the Suir Estuary were compared with studies elsewhere in Ireland and Europe (Chapter 7). Cu concentrations were low (range 5.0 – 10.0 mg $kg^{-1}$ in *F. vesiculosus*) when compared with other estuaries in Ireland and elsewhere in Europe (Cullinane & Whelan 1982; Barnett & Ashcroft, 1985; Langston, 1986; Miramand & Bentley, 1992; Molloy & Hills, 1996; Carvalho *et al.*, 1997; Martin *et al.*, 1997; O'Leary & Breen, 1998). However, Pb concentrations in Suir Estuary seaweed species were very high (range: below limits of detection to 34.7 mg $kg^{-1}$ in *F. vesiculosus*) even when compared to heavily industrialized sites in Britain and were similar to levels recorded in the Tagus Estuary which is heavily polluted by ship building and smelting industries (Carvalho *et al.*, 1997). The high concentration of Pb in *F. vesiculosus* at Johns River (34.7 mg $kg^{-1}$) was confirmed by high concentrations in midlittoral sediments (63.4 mg $kg^{-1}$) at the same site. These findings indicate a substantive pollution source, or sources, of Pb upstream on Johns River.

Seaweed species differ in their capacity to accumulate metals. In this study *Polysiphonia lanosa* contained the highest concentrations of metals of the seaweed species examined, including that of its host *A. nodosum* (Chapter 7). More research is required to investigate the reasons behind this enhanced accumulation of metals by *P. lanosa* and what influence the host-hemiparasite relationship might have on the uptake.

Sediments are probably the most widely used compartment for monitoring of metal concentrations in estuaries (Salomons, 1985; Bryan & Langston 1992; Fletcher *et al.*, 1994; Neill, 1998; Harland *et al.*, 2000). Higher concentrations of Cr were recorded in midlittoral sediments than in salt marsh plants or seaweeds (Chapter 5, Chapter 6 and Chapter 7) and this would seem to indicate that it is mainly Cr(III), the less biologically active (and less toxic) form, which is present in the Suir Estuary. The trivalent form is normally associated with anthropogenic sources and is further evidence of Cr pollution (Bryan & Langston, 1985). A major drawback to the use of sediments for monitoring purposes is that the results may bear little relation to the levels that are biologically available (Bryan *et al.*, 1985). Also, the preparation, digestion and analysis of sediment material is time consuming, particularly as fraction size and organic matter content also need to be determined (Chapter 3 and Chapter 5). Despite the drawbacks of sediments for monitoring metal pollution, sediments can readily be sampled along the full length of the estuary and give an additional perspective to metal concentrations in biotic species. Sediment concentrations are an essential component of estuarine pollution indices devised by Wilson & Jeffrey (1987).

Although the preparation of water samples for metal analysis is less time consuming compared to sediments or biotic species, the difficulties during analysis are much greater. The very low concentrations ($\mu g\ l^{-1}$) are further complicated by interference with certain metals by salt ions in the estuary water, during AA spectrophotometer (graphite furnace) analysis. This was particularly the case with Pb in this study, and several chemical modifiers were tried (Chapter 3). The high degree of intra-site variability in water metal concentrations recorded in this study makes comparisons with other compartments in the estuary, and with other estuaries, less reliable.

The two biotic sample types investigated in this research were seaweeds and salt marsh vegetation. They have an important advantage over abiotic samples because they reflect the availability of particular pollutant chemicals in the water medium for uptake by biota (Bryan *et al.*, 1985). These plant and macroalgae species, therefore, can be valuable tools for comparative monitoring of metal loadings between estuaries, between sites in estuaries, and between years. But care has to be taken that sampling is carried out at the same time of year as this has a major influence on metal accumulation in salt marsh plants (Otte *et al.*, 1991; Williams *et al.*, 1994a; Caçador *et al.*, 2000), and in seaweed species (Miramand & Bentley, 1992; Stengel & Dring, 2000). A range of environmental factors like salinity, flooding frequency, pH, organic matter content, must be taken into account when making comparisons of metal concentrations (Chapters 5, 6, 7).

Phillips (1994) summarised a number of pre-requisites for a species to act as an efficient biomonitor of trace contaminants. They should be strong net accumulators of metals and reflect ambient bioavailabilities. They should also exhibit widespread geographical distributions and year-round availability; be easy to sample and to identify taxonomically and be tolerant of changes in salinity and turbidity. The salt marsh species *A. tripolium* complies well with these requirements, particularly because of its widespread distribution along the Suir Estuary (Chapter 4 and Chapter 6). Roots and shoots of *A. tripolium* need to be sampled and analysed separately for metals in order to allow for salinity effects on uptake, translocation and respiration. The two seaweed species, *F. vesiculosus* and *P. lanosa* also comply well with the requirements for efficient biomonitors (Chapter 4 and Chapter 7). *Fucus vesiculosus* has the advantage of widespread distribution in the middle and high salinity sites; *Polysiphonia lanosa* has the advantage of low intra-site variation in metal concentrations. Analysis of the mature thallus in the seaweed species gives the best longer-term bioaccumulation of metals e.g. one year (Bryan et al., 1985).

Data collected from the various compartments in this study, (including the data summarised in Figure 2), can be used in the management of environmental quality of the Suir Estuary:

- Although the metal concentrations recorded during the study were below the Water Quality Standards set by the Water Quality Management Plan for the Suir/Barrow/Nore Estuary (Carlow County Council *et al.*, 1990), the relatively high Pb concentrations (by comparison with other European estuaries) at Johns River and the elevated Cr concentrations in the upper Suir Estuary, are particular causes for concern. These pollution sources need to be remedied.

- An on-going monitoring programme for Pb and Cr concentrations in the Suir Estuary needs to be put in place as a matter of urgency. Biotic species better reflect the uptake of metals by other species in the estuarine system. The seaweed species *F. vesiculosus* and *P. lanosa,* as well as the salt marsh plant, *A. tripolium,* are recommended for biomonitoring based on results from this study.

- If resources allow, then midlittoral sediments should also be analysed. This can be particularly important in the case of metals such as Cr that are readily adsorbed on to sediment particles.

- If resources allow, multiple samplings of biotic species and sediments is recommended, e.g. four times per year to allow for seasonal effects. However, if resources are limited then one sampling should be taken. The optimum time for sampling seaweeds is winter or early spring and midlittoral sediments can also be sampled at this time. The optimum time for a single sampling of *Aster tripolium* is September-October when the highest concentrations of metals are generally present (Otte, 1991).

- Comparisons of metal loadings in the biotic species can be made from site to site within the Suir Estuary, between the Suir Estuary and other estuaries in Ireland or elsewhere, and between years. In the same way, midlittoral sediments can also be used for comparison purposes.

- A number of other metals should also be monitored, including Cd, Hg and Sn (following the prevalence of tributyltin oxide on boats and ships). These three metals are of particular envirotoxicological significance.

- Land development (principally salt marsh infill), is a major threat to the Suir Estuary. This threat will grow as pressure increases from Waterford City, and its environs, to expand. This could have long-term implications for the viability of the salt marsh habitats on the estuary.

The principal aims of the research in this study, (as outlined in Chapter 1), were achieved:

1. The lower salt marsh vegetation and midlittoral seaweed species were described at six sites and five sites, respectively, along the Suir Estuary in 1995 and 1996. These descriptions formed the basis for further research into metal concentrations in salt marsh plants and seaweed species.

2. Cu, Pb and Cr concentrations in midlittoral and salt marsh sediments were recorded at eight sites on the Suir Estuary in 1997 and 1998. Comparisons were made of metal concentrations between sites and between midlittoral sediments and salt marsh sediments.

3. Concentrations of Cu and Pb in a number of monocotyledon and dicotyledon salt marsh species were investigated. The effects of salinity on the partitioning of these metals between above-ground and below-ground plant parts was observed, notably in *A. tripolium.*

4. Concentrations of Cu, Pb and Cr were determined in three brown (Phaeophyta) seaweed species; *Fucus vesiculosus, F. serratus* and *Ascophyllum nodosum*, as well as one red (Rhodophyta) seaweed species, *Polysiphonia lanosa,* at five sites along the Suir Estuary in 1998. Comparisons were made of metal concentrations in *A. nodosum* and its hemiparasite, *P. lanosa,* as well with the other seaweed species. Metal concentrations in surface estuary water were also determined and compared with concentrations in seaweeds.

5. *Aster tripolium* was identified as the most suitable salt marsh species for the biomonitoring of metals. This was primarily because of its widespread distribution along the Suir Estuary. However, roots and shoots must be sampled and analysed separately because of differential partitioning of Pb between roots and shoots under changing salinity levels.

   *Fucus vesiculosus* and *P. lanosa* were identified as suitable seaweed species for biomonitoring. *Fucus vesiculosus* is recommended because of its widespread distribution along the Suir Estuary while *Polysiphonia lanosa* is recommended because of the low intra-site variation.

6. Based on the research carried out during this study a number of recommendations were made for the management of metal pollution in the Suir Estuary.

Arising from this study a number of areas for further research are proposed:

1. As part of an on-going monitoring programme of metal pollution on the Suir Estuary, some additional metals, principally Cd, Hg and Sn, should be investigated.

2. The influence that the hemiparasitic relationship between *Ascophyllum nodosum* and *Polysiphonia lanosa* has on the accumulation of metals in both seaweed species should be examined.

3. Investigation of the higher accumulation of metals by *P. lanosa* compared to the other seaweed species should be carried out. It is also proposed that research be done into the potential of *P. lanosa* as a biofiltration agent for the removal of metals from waste streams because of its relatively high bioaccumulation potential.

4. More detailed investigation be carried out into the differences in metal adsorption between midlittoral sediments and salt marsh sediments on the Suir Estuary and the role of organic matter in this adsorption.

# Summary

Populations of monocotyledonous and dicotyledonous plants were recorded along the lower salt marsh zone and populations of midlittoral seaweed species were recorded along the midlittoral zone of the Suir Estuary. These descriptions formed the basis for further research into metal concentrations in these salt marsh plants and seaweeds.

Concentrations of Cu and Pb were recorded in the roots and shoots of salt marsh plants. The main concentrations of Pb were recorded in the roots of monocotyledons, while in dicotyledons Pb was mainly concentrated in the shoots. In contrast, higher Cu concentrations were recorded in the roots of all monocotyledons and dicotyledons examined, except *Spartina* spp.. This study showed that with increasing salinity, the uptake of Pb from the soil by *A. tripolium* increased and there was a direct gradient in metal concentration from the roots to aerial parts of the plant. At low salinity sites Pb accumulated only in the roots whereas at higher salinity sites there was a marked translocation to the leaves. By contrast, Cu concentrations in the roots remained higher than in shoots at high salinity sites. There was a significant inverse correlation between Cu concentrations in the sediment and *A. tripolium* shoots, as salinity increased. *Aster tripolium* is recommended as a bioindicator species for metal pollution, principally because of its widespread distribution along the Suir Estuary. Roots and shoots must be sampled and analysed separately because of differential partitioning of Pb between roots and shoots, under changing salinity levels.

Metal concentrations in seaweed species on the Suir Estuary were compared with studies elsewhere in Ireland and Europe. Overall, Cu and Cr concentrations were low when compared with other estuaries. However, Pb concentrations in Suir Estuary seaweed species were very high even when compared to heavily industrialized sites in Britain and elsewhere in Europe. Seaweed species differ in their capacity to accumulate metals. In this study the hemiparasite, *Polysiphonia lanosa,* contained the highest concentrations of metals of the seaweed species examined, including that of its host *Ascophyllum nodosum.* More research is required to investigate the reasons behind this enhanced accumulation of metals by *P. lanosa* and what influence the host-hemiparasite relationship might have on the uptake. Concentration factors of approximately $10^3$ in seaweed species, over metal levels in water, were recorded in this study. Two seaweed species are recommended for biomonitoring purposes; *F. vesiculosus* because of its widespread distribution along the estuary and *P. lanosa* because of low intra-site variation in metal concentration.

Concentrations of Cu, Pb and Cr were recorded in salt marsh sediments and midlittoral sediments. Concentrations of Cu, Pb and Cr in midlittoral sediments were significantly higher in the upper Suir Estuary compared to the lower estuary. Elevated Pb concentrations in midlittoral sediments at the mouth of Johns River strongly indicated a pollution source upstream on that tributary and this evidence was supported by high Pb concentrations in the seaweed species, *Fucus vesiculosus,* also at this site. Elevated Cr concentrations in midlittoral sediments and in *F. vesiculosus* and *Aster tripolium* (roots) in the vicinity of Johns River and Maypark indicated a source of Cr pollution in that area of the estuary. The relatively high concentrations of Cr recorded in midlittoral sediments at Granagh were most likely as a result of historical pollution from old tanneries upstream.

Data collected during this study can be used in the management of environmental quality of the Suir Estuary. The metal concentrations recorded were below the Water Quality Standards set by the Water Quality Management Plan (1990) for the Suir/Barrow/Nore Estuary. However, there is no room for complacency, particularly in relation to the Pb and Cr concentrations recorded at Johns River and elsewhere in the upper estuary. A number of other metals should be investigated as a matter of urgency. Chief among these are Cd, Hg and Sn as these metals are of particular envirotoxicological significance.

## ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. Suresh Nesaratnam, my supervisor based at The Open University, Milton Keynes, for his guidance and support throughout this study.

I also wish to sincerely thank Dr. Joe Caffrey, my regional (Ireland) supervisor, whose friendship and encouragement, as well technical expertise, I valued deeply during the course of this study.

My thanks to Professor Andrew Porteous, Department of Environmental and Mechanical Engineering, Open University, for making this study possible. Thanks also to Dr. Ian Stevenson, Open University, Ireland, for his help in the initial stages of the study.

A special word of thanks to Dr. Peter McLoughlin, Waterford Institute of Technology, for his advice and encouragement during long hours of AA spectrophotometer analysis.

My thanks also, to Dr. Eric Martin, School of Science, Waterford Institute of Technology, for allowing me access to research facilities.

A special word of thanks to my Open University students, Seamus Dunne, Michael O'Leary, Pat Dwyer, Pat Tarrant, Colin Foley, and others, for their assistance and good humour during the course of this study. I also wish to thank my brother John and my daughter Rosemary for their help in the field. Thanks also to Brandy for his company on the estuary.

I wish to thank Dr. Matthew Jebb, of the National Botanic Gardens for identifying and confirming the identity of plant specimens.

I wish to express my appreciation to Captain Philip Cowman, Harbour Master, and other staff at Waterford Harbour, for their advice and access to charts.

Finally, I wish to express my sincere gratitude to my wife, Mary, and our daughters, Ruth, Rosemary and Ciara for their love and patience during the course of this study.

# REFERENCES


Adam, P. (1990). *Saltmarsh Ecology.* Cambridge University Press, Cambridge. 461pp.

APHA Standard Methods (1992). *Standard Methods for the Examination of Water and Wastewater.* American Public Health Association, 18th ed.: 4-49.

Attrill, M. J. & Thomes, R. M. (1995). Heavy metal concentrations in sediment from the Thames Estuary, UK. *Mar. Pollut. Bull.*, **30**: 742-744.

Barnett, B. E. & Ashcroft, C. R. (1985). Heavy metals in *Fucus vesiculosus* in the Humber estuary. *Environ. Pollut.*, **9**: 193-213.

Beeftink, W. G., Nieuwenhuize, J., Stoeppler, M. & mohl, C. (1982). Heavy metal accumulation in salt marshes from the Eastern and Western Scheldt. *Sci. Total Environ.*, **25**: 199-223.

Beeftink, W. G. (1985). Vegetation study as a generator for population biological and physiological research on salt marshes. *Vegetatio*, **62**: 469-486.

Betty, N. G., Turner, A., Tyler, A. O., Falconer, R. A. & Millward, G. E. (1996). Modelling contaminant geochemistry in estuaries. *Wat. Res.*, **30**: 63-74.

Bowman, J. J., Clabby, K. J., Lucey. J., Mccarrigle, M. L. & Toner, P. F. (1996). *Water Quality in Ireland 1991-1994.* Environmental Protection Agency, Wexford.75pp.

Bradley, J. & Halpin, A. (1992). The topographical development of Scandanavian and Anglo-Norman Waterford City. In: *Waterford History & Society*, (eds.) W. Nolan & T. Power, Geography Publications, Dublin. 105-130.

Bryan, G. W. (1969). The absorption of zinc and other metals by the brown seaweed Laminaria digitata. *J. Mar. Biol. Ass. UK.* **49**: 225-243.

Bryan, G. W. & Hummerstone, L. G. (1973). Brown seaweed as an indicator of heavy metals in estuaries in south-west England. *J. Mar. Biol. Ass. U.K.*, **53**: 705-720.

Bryan, G. W., Langston, W. J., Hummerstone, L. G. & Burt, G. R. (1985). *A Guide to the Assessment of Heavy-Metal Contamination in Estuaries using Biological Indicators*. Mar. Biol. Ass. U.K., Occas. Public., number 4, 1-34.

Bryan, G. W. & Langston, W. J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environ. Pollut.*, **76**: 89-131.

Bubb, J. M. & Lester, J. N. (1991). The impact of heavy metals on lowland rivers and the implications for man and the environment. *Sci. Total Environ.*, **100**: 207-233.

Butcher, D. J. & Sneddon, J. (1998). *A Practical Guide to Graphite Furnace Atomic Absorption Spectrometry*, John Wiley & Sons, New York. 250pp.

Caçador, I., Vale, C. & Catarino, F. (2000). Seasonal variation of Zn, Pb, Cu and Cd concentrations in the root-sediment system of *Spartina maritima* and *Halimione portulacoides* from Tagus estuary salt marshes. *Mar. Environ. Res.*, **49**: 279-290.

Cameron, W. M. & Pritchard, D. W. (1963). Estuaries. In: *The Sea*, Vol. 2, (ed) M. N. Hill. Wiley, New York. pp324.

Carlow County Council, Kilkenny County Council, Tipperary S. R. County Council, Waterford County Council, Waterford Corporation and Wexford County Council. (1990). *Water Quality management Plan for the Suir/Barrow/Nore Estuary*, Kilkenny. pp122.

Carvalho, M. L., Ferreira, J. G., Amorim, P., Marques, I. M. & Ramos, M. T. (1997). Study of heavy metals and other elements in macrophyte algae using energy-dispersive x-ray fluorescence. *Environ. Toxic. & Chem.*, **16**: 807-812.

Ciciottte, S. L. & Thomas, R. J. (1997). Carbon exchange between *Polysiphonia lanosa* (Rhodophyceae) and its brown algal host. *Amer. J. Bot.*, **84**: 1614-1616.

Clark, R. B. (1989). *Marine Pollution*, Clarendon Press, Oxford. pp212.

Codling, I. D., Nixon, S. C. & Platt, H. M. (1991). *An Assessment of the Biological Status of Intertidal Sediments.* National Rivers Authority, London. 121pp.

Crist, R.H., Oberholser, K., McGarrity, J., Crist, D.R., Johnson, J. K. & Brittsan, J.M. (1992). Interaction of metals and protons with algae. 3. Marine algae, with emphasis on lead and aluminium. *Environ. Sci. Technol.*, **26**: 496-502.

Cullinane, J. P. & Whelan, P. M. (1982). Copper, cadmium and zinc in seaweeds from the south coast of Ireland. *Mar. Pollut. Bull.*, **13**: 6, 205-208.

Curtis, T. G. F. & Sheehy Skeffington, M. J. (1998). The salt marshes of Ireland: an inventory and account of their geographical variation. *Biology and Environment: Proceedings of the Royal Irish Academy*, **98B**: 87-104.

Dixon, P. S. & Irvine, L. M. (1977). *Seaweeds of the British Isles. Vol. Rhodophyta.* British Museum, London. 252pp.

Doyle, M. O. & Otte, M. L. (1997). Organism-induced accumulation of iron, zinc and arsenic in wetland soils. *Environ. Pollut.*, **96**: 1-11.

Eide, I., & Myklestad, S. (1980). Long-term uptake and release of heavy metals by *Ascophyllum nodosum* (L.) Le Jol. (Phaeophyceae) in situ. *Environ. Pollut.*, **23**: 19-28.

Elliott, H. A., Liberati, M. R. & Huang, C. P. (1986). Competitive adsorption of heavy metals by soils. *J. Environ. Qual.*, **15**: 214-219.

European Union. (1989). European Communities (Quality of Surface Water) Regulations, 1989, (S.I. No. 75/440/EEC).

Evans, G. P. (1993). *Marine and Estuarine Modelling: Current Practice in the UK.* Foundation for Water Research, Marlow. 21pp.

Flanagan, M. J. (1989). *Aqueous-sedimentary interaction in the estuary of the river Suir with particular reference to chromium and lead.* PhD thesis, Trinity College, University of Dublin, Volume 1: 475pp.

Fletcher, C. A., Bubb, J. M. & Lester, J. N. (1994). Magnitude and distribution of anthropogenic contaminants in salt marsh sediments on the Essex coast, UK. II. Selected metals and metalloids. *Sci. Total Environ.*, **155**: 47-59.

Forsberg, A., Soderland, S., Frank, A.,Petersson, L. R. & Pedersen, M. (1988). Studies on metal content in the brown seaweed, *Fucus vesiculosus*, from the Archipelago of Stockholm. *Environ. Pollut.*, **49**: 245-263.

Förstner, U. & Salomons, W. (1980). Trace metal analysis on polluted sediments. 1. Assessment of sources and intensities. Environ. Technol., Letts. **1**. 494-505.

Foster, P. (1976). Concentrations and concentration factors of heavy metals in brown algae. *Environ. Pollut.*, **10**: 45-53.

Fowler, J. & Cohen, L. (1990). *Practical Statistics for Field Biology*, John Wiley & Sons, Chichester. 227pp.

Fralick, R. A. & Mathieson, A. C. (1975). Physiological ecology of *Polysiphonia* species. *Mar. Biol.* **29**: 29-36.

Fuge, R. & James, K. H. (1973). Trace metal concentrations in brown seaweeds, Cardigan Bay, Wales. *Mar. Chem.* **1**: 281-293.

Fuge, R. & James, K. H. (1974). Trace metal concentrations in *Fucus* from the Bristol Channel. *Mar. Pollut. Bull.*, **5**: 9-12.

Garbary, D. J., Burke, J. & Lining, Tian. (1991). The *Ascophyllum /Polysiphonia /Mycosphaerella* symbiosis. 11. Aspects of the ecology and distribution of Polysiphonoa lanosa in Nova Scotia. *Bot. Mar.*, **34**: 391-401.

Gekeler, W. Grill, E., Winnaker, E. & Zenk, M. (1988). Algae sequester heavy metals via synthesis of phytochelatin complexes. *Arch. Microbiol.*, **150**: 197-202.

Gleason, M. L., Drifmeyer, J. E. & Zieman, J. C. (1979). Seasonal and environmental variation in Mn, Fe, Cu, and Zn content of *Spartina alterniflora. Aquat. Bot.* **7**: 385-392.

Harland, B. J., Taylor, D. & Wither, A. (2000). The distribution of mercury and other trace metals in the sediments of the Mersey Estuary over 25 years 1974-1998. *Sci., Total Environ.*, **253**: 45-62.

Ho, Y. B. (1984). Zn and Cu concentrations in *Ascophyllum nodosum* and *Fucus vesiculosus* (Phaeophyta, Fucales) after transplantation to an estuary contaminated with mine wastes. *Conserv. Recycling*, **7**: 329-337.

Huiskes, A.H.L. & Nieuwenhuize, J. (1985). Uptake of heavy metals from contaminated soils by salt marsh plants. In; *Proc. 5th Int. Conf. On 'Heavy Metals in the Environment'*, Heidelberg (ed. CEP Consultants Ltd), pp 307-309. Edinburgh, UK.

Ingle, J. D. & Crouch, S. R. (1988). *Spectrochemical Analysis*, Prentice Hall, New Jersey. 590pp.

Jeffrey, D. W., Wilson, J. G., Harris, C. R. & Tomlinson, D. L. (1985). The application of two simple indices to Irish estuary pollution status. In *Estuarine Management and Quality Assessment*, (ed.) J. G. Wilson & W. Halcrow, Trinity College, University of Dublin, pp. 147-161.

Jeffrey, D. W., Madden, B., Rafferty, B., Dwyer, R., Wilson, J., & Allott, N. (1992). *Dublin Bay Water Quality Management Plan: Algal Growths and Foreshore Quality*. Environmental Research Unit, Dublin. 168pp.

Kumar, H. D. & Singh, H. N. (1979). *A Textbook on Algae*. Macmillan Press Ltd. 216pp.

Langston, W. J. (1986). Metals in sediments and benthic organisms in the Mersey estuary. *Estuarine Coastal Shelf Sci.*, **23**: 239-261.

Leal, M. C. F. Vasconcelos, M. T. Sousa-Pinto, I. & Cabral, J. P. S. (1997). Biomonitoring with benthic macroalgae and direct assay of heavy metals in seawater of the Oporto coast (northwest Portugal). *Mar. Pollut. Bull.*, **34**: 1006-1015.

Levin, P. S. & Mathieson, A. C. (1991). Variation in a host-epiphyte relationship along a wave exposure gradient. *Mar. Ecol. Prog*, Ser., **77**: 271-278.

Lewis, J. R. (1964). *The Ecology of Rocky Shores*, Hodder & Stoughton. 323pp.

Liu, Y. P., Millward, G. E. & Harris, J. R. W. (1998). Modelling the distributions of dissolved Zn and Ni in the Tamar Estuary using hydrodynamics coupled with chemical kinetics. *Estuarine Coastal Shelf Sci.*, **47**: 535-546.

Lobban, C. S. & Harrison, P. J. (1997). Seaweed Ecology and Physiology. Cambridge University Press, Cambridge. 366pp.

Loring, D. H. & Prosi, F. (1986). Cadmium and lead cycling between water, sediment, and biota in an artificially contaminated mud flat on Borkum (F.R.G.). *Wat. Sci. Tech.* **18**: 131-139.

Luoma, S. N., Bryan, G. W. & Langston, (1982). Scavenging of heavy metals from particulates by brown seaweed. *Mar. Pollut. Bull.* **13**: 11, 394-396.

McLuskey, D. S. (1989). *The Estuarine Ecosystem.* Blackie Academic & Professional, Glasgow. 215pp.

Mantoura, R. F. C., Dickson, A. & Riley, J. P. (1978). The complexation of metals with humic materials in natural waters. *Estuarine & Coastal Mar. Sci.*, **6**: 387-408.

Marschner, H. (1995). *Mineral Nutrition of Higher Plants*, Academic Press. 889pp.

Martin, M. H., Nickless, G. & Stenner, R. D. (1997). Concentrations of cadmium, lead, nickel and zinc in the alga *Fucus serratus* in the Severn estuary from 1971 to 1995. *Chemosphere,* **34**: 2, 325-334.

MathSoft (1996). *Axum Technical Graphics and Data Analysis*, MathSoft Inc., Cambridge, Massachusetts. 370pp.

Meyerson, A. L., Luther, G. W. Krajewski, J. & Hires, R. I. (1981). Heavy metal distribution in Newark Bay Sediments. *Mar. Pollut., Bull.* **12**: 244-250.

Millward, G. E., Glegg, G. A. & Morris, A. W. (1992). Zn and Cu removal kinetics in estuarine waters. *Estuarine, Coastal and Shelf Sci.*, **35**: 37-54.

Miramand, P. & Bentley, D. (1992). Heavy metal concentrations in two biological indicators (*Patella vulgata* and *Fucus serratus*) collected near the French nuclear fuel reprocessing plant at La Hague. *Sci. Total Environ.*, **111**: 135-149.

Molloy, F. J. & Hills, J. M. (1996). Long-term changes in heavy metal loadings of *Ascophyllum nodosum* from the Firth of Clyde, UK. *Hydrobiologia*, **326/327**: 305-310.

Morris, A. W. & Bale, A. J. (1975). The accumulation of cadmium, copper, manganese and zinc by *Fucus vesiculosus* in the Bristol Channel. *Estuarine Coastal Shelf Sci.* **3**: 153-163.

Munda, I. M. (1982). The effect of different pollutants on benthic marine algae, In: *Proc. Journ. Etud. Pollut*, Cannes, C.I.E.S.M., **V1**: 721-726.

Mwanuzi, F, & De Smedt, F. (1999). Heavy metal distribution model under estuarine mixing. *Hydrol. Process.*, **13**: 789-804.

Neill, M. (1998). *A Report on Water Quality in the Suir/Barrow/Nore Estuary 1997*. Environmental Protection Agency, Kilkenny. 29pp

Nham, T. T. (1989). Direct determination of As, Cu and Pb in seawater by Zeeman graphite furnace atomic absorption spectrometry. *Varian Instruments at Work*, AA-**92**: 1-4.

O'Leary, C. & Breen, J. (1998). Seasonal variation of heavy metals in *Mytilus edulis*, *Fucus vesiculosus* and sediment from the Shannon Estuary. *Biology and Environment: Proceedings of the Royal Irish Academy*, **98B**: 153-169.

Otte, M. L. (1991). *Heavy metals and arsenic in vegetation of salt marshes and floodplains*. PhD Thesis, Centrale Huisdrukkerij Vrije Universiteit, Amsterdam.

Otte, M. L. (2001). What is stress to a wetland plant? *Envir. and Exper. Bot.*, **46**: 195-202.

Otte, M. L., Rozema, J., Koster, L., Haarsma, M. S. & Broekman, R. A. (1989). Iron plaque on roots of *Aster tripolium* L.: interaction with zinc uptake. *New Phytol.*, **111**: 309-317.

Otte, M. L., Bestebroer, S. J., van der Linden, J. M., Rozema, J. & Broekman, R. A. (1991). A survey of zinc, copper and cadmium concentrations in salt marsh plants along the Dutch coast. *Environ. Pollut.*, **72**: 175-189.

Otte, M. L., Haarsman, M. S., Broekman, R. A. & Rozema, J. (1993). Relation between heavy metal concentrations in salt marsh plants and soil. *Environ. Pollut.*, **82**: 13-22.

Paucot, H., & Wollast, R. (1997). Transport and transformation of trace metals in the Scheldt estuary. *Mar. Chem.*, **58**: 229-244.

Penot, M. & Hourmant, A. & Penot, M. (1993). Comparative study of metabolism and forms of transport of phosphate between *Ascophyllum nodosum* and *Polysiphonia nodosum*. *Physiol. Plant.*, **87**: 291-296.

Phillips, D. J. H. (1977). The use of biological indicator organisms to monitor trace element pollution in marine and estuarine environments – a review. *Environ. Pollut.*, **13**: 281-317.

Phillips, D. J. H. (1994). Macrophytes as biomonitors of trace metals. In: *Biomonitoring of Coastal Waters and Estuaries*, (ed.) K. J. M. Kramer, CRC Press Inc., Boca Raton. FL, pp327.

Pritchard, D. W. (1967). What is an estuary: a physical viewpoint. In: G. H. Lauff (ed.) *Estuaries*, American Association for the Advancement of Science, Public. No. 83, pp3-5.

Raffaelli, D. & Hawkins, S. (1996). *Intertidal Ecology*. Chapman & Hall, London. 337pp.

Ragan, M.A. Smidrød, O. & Larsen, B. (1979). Chelation of divalent metal ions by brown algal polyphenols. *Mar. Chem.*, **7**, 265-271.

Reboredo, F. (1993). How differences in the field influence Cu, Fe and Zn uptake by *Halimione portulacoides* and *Spartina maritima*. *Sci. Total Environ.*, **133**: 111-132.

Riget, F., Johansen, P. & Asmund, G. (1995). Natural seasonal variation of cadmium, copper, lead and zinc in brown seaweed (*Fucus vesiculosus*). *Mar. Pollut. Bull.*, **30**: 6, 409-413.

Riget, F., Johansen, P. & Asmund, G. (1997). Baseline levels and natural variability of elements in three seaweed species from west Greenland. *Mar. Pollut. Bull.*, **34**: 3, 171-176.

Robinson, N.J. (1989). Algal metallothioneins; secondary metabolites and proteins. *App. Phycology*, **1**: 5-18.

Rozema, J., Bijwaard, P., Prast, G. & Broekman, R. (1985). Ecophysical adaptations of coastal halophytes from foredunes and salt marshes. *Vegetatio*, **62**: 499-521.

Rozema, J., Otte, M. L., van Schie, C. & Ernst, W. H. O. (1988). Foliar uptake of heavy metals by estuarine plants in response to contaminated sea water flooding. In: Orio, A. A. (ed.), *Proc. Int. Conf. Environmental Contamination*, Venice, CEP Consultants, Edinburgh, pp73-75.

Rozema, J., Otte, M. L., Broekman, R., Kamber, G. & Punte, H. (1990). The response of *Spartina anglica* to heavy metal pollution. In: *Spartina anglica – A Research Review*, HMSO, London. pp63-68.

Salomons, W. (1980). Adsorption processes and hydrodynamic conditions in estuaries. *Environ. Technol. Letts.*, **1**: 356-365.

Salomons, W. (1985). Sediments and water quality. *Env. Technol. Lett.*, **6**, 315-326.

Schonbeck, M.W. & Norton, T. A. (1980). Factors controlling the lower limits of fucoid algae on the shore. *J. Exp. Mar. Biol and Ecol.*, **43**: 131-150.

Seeliger, U. & Edwards, P. (1977). Correlation coefficients and concentration factors of copper and lead in seawater and benthic algae. *Mar. Pollut. Bull.* **8**: 16-19.

Smith, K.L., Hann, A.C. & Harwood, J.L. (1986). The subcellular localization of absorbed copper in *Fucus. Physiol. Plant.* **66**; 692-698.

Stace, C. (1991). *New Flora of the British Isles.* Cambridge University Press, Cambridge. 1226pp

Stengel, D. B. & Dring, M. J. (2000). Copper and iron concentrations in *Ascophyllum nodosum* (Fucales, Phaeophyta) from different sites in Ireland and after culture experiments in relation to thallus age and epiphytism. *J. Exp. Mar. Biol. & Ecol.*, **246**: 145-161.

Sundby, B., Vale, C., Cacador, I., Catarino, F., Madureira, M. J. & Caetano, M. (1998). Metal–rich concreations on the roots of salt marsh plants: Mechanism and rate of formation. *Limnol. Oceanogr.*, **43**: 245-252.

Teasdale, P. R., Batley, G. E., Apte, S. C. & Webster, I. T. (1995). Pore water sampling with sediment peepers. *Trends in Analytical Chemistry*, **14**, 250-256.

Tomlinson, D. L., Wilson, J. G., Harris, C. R. & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer Meeresunters.*, **33**: 566-575.

Toth, G. & Pavia, H. (2000). Lack of phlorotannin induction in the brown seaweed *Ascophyllum nodosum* in response to increased copper concentrations. *Mar. Ecol. Prog. Ser.*, **158**: 111-119.

Turner, H. G. H. & Evans, L. V. (1977). Physiological studies on the relationship between *Ascophyllum nodosum* and *Polysiphonia lanosa. New Phytol.*, **79**: 363-371.

Ungar, I. A. (1998). Are biotic factors significant in influencing the distribution of halophytes in saline habitats? *The Botanical Review*, **64**: 176-199.

US Geological Survey. (1979). *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments,* Book 5. 748pp.

Webb, D. A. (1967). *An Irish Flora.* Dundalgan Press, Ltd, Dundalk. 259pp.

Williams, T. P., Bubb, J. M. & Lester, J. N. (1994a). Metal accumulation within salt marsh environments: a review. *Mar. Pollut. Bull.* **28**: 277-290.

Williams, T. P., Bubb, J. M. & Lester, J. N. (1994b). The occurrence and distribution of trace metals in halophytes. *Chemosphere*, **28**: 1189-1199.

Wilson, J. G. (1988). *The Biology of Estuarine Management.* Croom Helm, London. 198pp.

Wilson, J. G. & Jeffrey, D. W. (1987). Europe-wide indices for monitoring estuarine quality. In: Biological indicators of pollution; D.H.S. Richardson (ed). *Proceedings of the Royal Irish Academy*, Dublin, 225-242.

Wright, D. J. & Otte, M. L. (1999). Wetland plant effects on the biogeochemistry of metals beyond the rhizosphere. *Biology and Environment*: *Proceedings of the Royal Irish Academy*, Dublin, **99B**: 3-10.

Wright, P. & Mason, C. F. (1999). Spatial and seasonal variation in heavy metals in the sediments and biota of two adjacent estuaries, the Orwell and the Stour, in eastern England. *Sci., Total Environ.*, **226**: 139-156.

Zedler, J. B., Callaway, J. C., Desmond, J. S., Vivian-Smith, G., Williams, G. D., Sullivan, G., Brewster, A. E. & Bradshaw, B. K. (1999). Californian salt-marsh vegetation: an improved model of spatial pattern. *Ecosystems*, **2**: 19-35.

Zwolsman, J G., Berger, G. W. & Van Eck, G. T. M. (1993). Sediment accumulation rates, historical input, postdepositional mobility and retention of major elements and trace elements in salt marsh sediments of the Scheldt estuary, SW Netherlands. *Mar. Chem.*, **44**: 73-94.

# LIST OF PUBLICATIONS

**Environmental Pollution** (*accepted for publication*):

Fitzgerald, E. J., Caffrey, J.M., Nesaratnam, S. T., McLoughlin, P.
Copper and lead concentrations in salt marsh plants on the Suir Estuary, Ireland.